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# THE USE OF SELENIUM OXYCHLORIDE AS A SOLVENT ON COAL

BY

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY  
SUPERVISION BY William Robert King, Jr.

ENTITLED The Use of Selenium oxychloride  
As a Solvent on Coal.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR  
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## THE USE OF SELENIUM OXYCHLORIDE AS A SOLVENT ON COAL.

### I. Introduction.

#### 1. General Nature of Coal Solvent Problem:

This investigation was taken up as part of a group of problems being studied in this laboratory involving numerous so-called solvents and reagents such as Benzene and Xylene under pressure, Diphenyl, Diphenyl ether, and Selenium oxychloride. The powerful corrosive and solvent action of selenium oxychloride has been known for several years, in fact it has been called by some " the universal solvent".

The question of coal solvents arose during the middle of the last century and has attained much prominence in the past decade until today the use of solvents is recognized as one of the four chief methods of attacking coal. It has long been realized that the results obtained from ordinary methods of analysis, such as proximate and ultimate, are of rather narrow application especially from a chemists point of view. The information derived from such analysis is rather for the engineer. It is such information which can be applied to engineering problems connected with the handling and use of coal such as purchase, storage, weathering, coking and ordinary combustion. These analyses give percentage results of the individual elements obtained by the destructive analysis of the coal, but they do not convey the slightest information relative to the actual organic constituents of coal as they occur in nature. It is not with percentages of hydrogen, carbon and oxygen or their compounds as produced by coking conditions and destructive analy-





sis that the chemist is fundamentally concerned, but with the unaltered compounds in coal as they occur in nature. It is with these constituents that the ultimate solution of such problems as distillation, combustion, carbonization, oxidation, weathering and storage lies. Here lies the field for microscopical and solvent work, particularly for solvents. If the coal conglomerate or any considerable part of it were to show preferential solubility in any given liquid solvent the chemist's problem would be greatly simplified.

The question of what kind of a solvent is most desired by chemists is hard to answer. A true solvent, as distinct from a reagent, should be chemically inert toward both the substance extracted and the residue. A solvent is wanted that will remove some part of coal, it matters not what, whether it be cellulosic, resinic, protein or waxes. Selective solvents are desired. Furthermore the coal constituents must be removed unchanged. Many so-called solvents largely used in recent years, such as phenol and pyridine, are open to the suspicion that results obtained by their use have been rather more than that due to a solvent action alone. The admitted difficulty then with most solvents is that they are reagents also.

There is yet a broader and more practical field for solvents. Thus far work with solvents on coal has not been of very great value relating to carbonization processes and it is to this end, that of practical application, that all coal problems should point. Solvents have been used more to learn of the composition of coal than to aid in the coking of it. It is very hard to link solvent work with carbonization. From the standpoint of carbonization it is the coking and non-coking constituents of coal which should be separated. Phenol and pyridine have been largely used in this attempt,



but it is doubtful if they have proved the right solvents for this purpose. To some extent they have proved successful as pointed out by Jones and Wheeler (1) (1914). Generally speaking however there has not yet been found a solvent which will separate out the coking from the non-coking constituent.

## 2. Historical and Theoretical:

A resume of the leading work with coal solvents and reagents follows.

De Marsilly (1862) (3) made what is probably the first comprehensive study of solvent action on coal. He treated various types of coal with alcohol, ether, carbon disulphide, benzene and chloroform at their boiling points. He noted that all except alcohol had a distinct solvent action on "fat" bituminous coals, chloroform having the most. Anthracite coals were not affected by these solvents. The treatment of good coking coals took away some of the coking property.

Guignet (1879) (4) used dry phenol at 110° and found that it was a better solvent for finely ground bituminous coal than was chloroform. The phenolic extract was a deep brown color and deposited brown flakes on cooling. Four percent of the coal was extracted.

Dondorff, according to Muck (1881) (5) extracted as high as 0.3 percent of some Westphalian gas coals with ether. The ethereal solution was at first fluorescent and after evaporation the extracted "resin" was not again entirely soluble in ether. Analysis of the extract showed in percent: C - 87.22; H - 9.2; O - 2.29; S - 1.29.

Reinsch (1885) (6) took the view that coal was composed of two substances which could be distinguished by action toward certain solutions. With alkaline solutions he isolated several substances which were not attacked by mineral acids.





Siepmann (1891) (7) made an important study of Westphalian coal by extraction with chloroform in a Soxhlet extractor. He obtained a deep brown solution with a green fluorescence. The extract equaled 1.25% of the coal. It was a heavy, dark brown solid with an odor like petroleum. He dissolved parts of the extract in ether, alcohol and chloroform. He also tried ether, alcohol and chloroform on fresh samples of the same coal. Analysis of the extracts was as follows:

	C.	H.	O.	N.	S.
Original coal.....	80.31	5.5	12.94		1.25
Composite chloroform extract	83.46	7.93	4.27	2.7	1.63
Crude ether extract .....	84.82	10.51	4.67	-	-
Redissolved ether extract .	78.74	9.64	11.60	-	-
Alcohol extract .....	72.52	10.08	17.40	-	-
Chloroform extract .....	78.82	8.56	9.97	-	2.65
Final coal residue .....	74.00	4.77	20.09		1.14

Watson Smith (1891) (8) tested the solubility of several cannel coals and a bituminous coal from Miiki, Japan, in benzene. Not more than one percent extraction was obtained from any of the cannel, but in the Mikke coal he got a ten percent extraction. He called the soluble extract "soluble bitumen" or petroleum. The extracted substance contained pyridine bases and phenol as well as hydrocarbons of the benzene series.

Anderson (1897) (9) treated some Scottish coals with gasoline and with carbon disulphide in the cold. He obtained results similar to Siepmann, but in contradiction to de Marsilly he noted no difference in the coking properties of coal before and after extraction.

Anderson and Roberts (1898) (10) treated an oxidized or weathered Scotch coal with dilute nitric acid and potassium hydroxide. A



number of substances of acidic nature were extracted. These were taken to be derivatives of humic acid. In regard to the coking property of a coal they attribute it to a certain substance in the coal which will volatilize or decompose easily. Nitrogen, sulfur, coking constituents of organic complexes, and small amounts of resinic materials are pointed out as being the main substances.

Baker (1901) (11) extracted finely divided coal with pyridine in a Soxhlet extractor for fifty hours at 110'-120'C. Two bituminous coals and an anthracite were so treated. The anthracite was not attacked to any degree. One bituminous gave 20.4% extraction, and the other 11.5%. The bituminous coals lost all or most of their coking properties after treatment.

Bedson (1908) (12) published results of further experiments with pyridine on gas coals. He showed that different constituents of coal contained various amounts of extractive material.

Anderson and Henderson (1902) (13) showed that the amount of volatile matter present in residues from pyridine extraction contained actually higher percents than the original coal. They stated that pyridine was the best solvent they had yet used. The percentage of C, H, and N in the extract was about the same as that in the original coals. The coking properties of a poor coal could be entirely removed, but was only partially removed from a strong coking coal.

Lewes (1912) (14) infers from this past work that from some coals pyridine dissolves everything but fixed carbon and the ash, and that the pyridine must attach itself to some constituent of the coal to form an additive compound insoluble in excess of pyridine. Lewes says "The resin constituents condition the coking of coal during destructive distillation, and they are of at least two kinds.





The first easily oxidizable, soluble in pyridine and saponifiable by alkalis, and which on weathering is oxidized into a humus body with evolution of water and carbon dioxide, and is responsible for the heating of coal in storage. The second class is non-oxidizable, not saponified by alkalis, and forms with pyridine a compound insoluble in excess of the reagent, and this class may be the hydrocarbons from the decomposed resins, as the residue in which they are present yield rich liquid hydrocarbons, a tar and pitch, but not much gas." Thus pyridine is not suitable for a solvent according to Lewes.

Stopes and Wheeler (1918) (15) contradict this conclusion of Lewes by saying that the amount of volatile matter yielded depends upon the temperature, duration, manner of heating, state of division and texture of the coal sample, all of which extraction of coal with pyridine greatly affects. They go on to state that retention of pyridine by coal has not yet been proven.

Frazer and Hoffman (1912) (16) worked on the constituents of coal soluble in phenol. Of all solvents investigated they reported phenol, pyridine and aniline as removing the largest quantities of soluble material. Phenol was selected for special study. For lack of contrary evidence they assume that coal substance soluble in phenol is present as such in the coal itself. They extracted in turn this substance with numerous solvents and reagents and believe that some of the substances isolated very closely approach pure compounds. For these they present molecular weights and C, H, and O analysis in several cases. A further study using pyridine was to be undertaken.

Burgess and Wheeler (1911) (17) made a very thorough investigation of the solvent action of pyridine on coal. Their results led to the establishment of the very definite theory that coal is com-



posed of two parts; first hydrogen yielding or cellulosic constituent, and second the paraffin yielding material. They illustrated their results by analyzing the gases given off at different temperatures in the destructive distillation of coal and try to show that the paraffin yielding or resinic constituents of coal break down first. This theory has later been proved erroneous by numerous investigators, among whom are-

Porter and Taylor (1916) (18) who, working for the bureau of mines, carried out similar work the unfortunately on weathered coals. They arrive at very different conclusions from Burgess and Wheeler. Their results, which are very accurate except for a few minor details, prove that the cellulosic material of coal is the first to decompose upon exposure to heat.

Pictet and Ramseyer (1911) (19) made a study of the solubility of gas coals in benzene. They succeeded in isolating hexahydrofluorene  $C_{13}H_{16}$ , which led to the conclusion that coals contain among other constituents polymerized hydroaromatic hydrocarbons. From the similarity of distillation products to fractions from petroleum distillation the authors conclude that coal and petroleum have a similar origin.

Wahl (1912) (20) introduced an improvement in experimental methods by mixing the coal to be extracted with some salt soluble in water.

Clark and Wheeler (1912) (21) extracted a bituminous coal with pyridine and then the extracted material with chloroform. They found that between 30-40% of the pyridine soluble material was soluble in chloroform or benzene. The analysis of their different fractions and of the original coal on the ash free basis is as follows-





	Original coal	-Insol.in Pyridine	-Soluble	-Sol.in both-
Carbon	82.92	80.81	77.32	85.33
Hydrogen	5.58	5.23	5.14	7.08
Oxygen	8.45	10.40	14.26	4.56
Nitrogen	1.35	2.14	2.07	1.71
Sulfur	1.70	1.42	1.21	1.32

These results are interesting from the standpoint of Nitrogen. If the investigators purified the residue and extract from pyridine and still get more Nitrogen than the original coal contained, it would seem as if the solvent had acted like a reagent toward some substance in the coal. Hybetic acid, waxes, and pure paraffins were found upon attempt to identify original coal substances.

Jones and Wheeler (1914) (22) obtained crystals of paraffin wax melting between 53'-59'C. by extracting with pentane that portion of the pyridine extract which was soluble in chloroform.

Stopes and Wheeler (1918) (23) worked with pyridine as a solvent and gave the following conclusions. That an accurate quantitative determination of the extracted material can be made only if the coal is ground fine and if both coal and pyridine is dry. Most of the extractive material was removed in twelve hours in a Soxhlet extractor. Small portions continue to be removed during several weeks. One difficulty met here as with other investigations, is that the coal, extract and residue will absorb oxygen in spite of all precautions, more slowly at low temperatures and faster at high temperatures. This oxygen forms in loose combination with certain parts of the coal material.

Pictet, Ramseyer and Kaiser (1916) (24) extracted five and one-half tons of Saare coal with boiling benzene for four days. From the extract they isolated several pure hydrocarbons both saturated and unsaturated.

Cherry (1919) (25) carried out a series of experiments to det-



emine the part played by oxygen. He extracted coal with phenol. The residue and extract were oxidized separately in various amounts and after mixing were submitted to carbonization. He showed that the residue or cellulosic constituent has the greatest avidity for oxygen. This cellulosic material if sufficiently oxidized will entirely prevent the mixture from coking. If the extract or resinic material is partly oxidized the bonding properties are greatly weakened.

Parr and Hadley (1915) (26) made a comprehensive study of phenol as a solvent on coal. They used a Soxhlet extractor and extracted the coal in absence of air by use of a stream of carbon dioxide. The temperature of the extraction was that of boiling toluene. Their results were: Coal varies as to type in the amount of soluble material. The higher volatile matter coals give the greatest extraction. Extraction of coal leaves a residue which will not coke. The coking constituent is in the extract. The residue and extract oxidize readily at room temperature, but most at 100°C. The residue shows the greatest avidity for oxygen. Residue and extract both show avidity for water, the residue showing the most. Volatile matter determinations show that the extract contains more than the residue. Ultimate analysis of coal, residue, and extract showed that percentages of hydrogen, oxygen, nitrogen and carbon were substantially the same. Destructive distillation of coal, residue and extract gave gases of practically the same composition.

Most of the work with solvents has been in extracting parts of coal soluble in organic solvents. All solvents tried have been neutral solvents, reagents, or oxidizing agents. The reagents and oxidizing agents change the coal. They dissolve the coal it is true, but destroy one part to obtain another. It is difficult to separate





the true solvents from the reagents in all cases. The following are the most widely used: benzene, gasoline, ethyl ether, benzene-toluene mixture, naphthalene, toluene, alcohol, anthracene, diphenyl, cresol, low boiling tar distillates, phenol-toluene mixture, and acetone all of which are considered more truly solvents; and carbon disulfide, chloroform, sodium hydroxide, nitric acid, ferric chloride, selenium oxychloride, pyridine, phenol, quinoline, aniline, sulfur dioxide, diphenyl ether, turpentine, ozone and potassium dichromate which are probably not such true solvents.

Fats, waxes, humic acids and in general so-called "resinic" materials have been separated from coal by solvent action. No solvent has yet been found for the "cellulosic" and protein parts of coal. These terms are here used in the general sense current in the literature today as originated by Prof. V. Lewes (2) of the University of Manchester (1911), to apply to the two main parts of coal as separated by solvents. The "cellulosic" is the residue not extracted and is supposed to be a degradation product of cellulose. The "resinic" is the extracted material which contains the coal resins. Since it is believed by some that gum or fossil resins are not a true constituent of coal it might be said that such solvents as phenol and pyridine, which extract this part, attack only a non-coal part and hence the true solvent for coal has not yet been found. Again, if nitrogen and sulfur, that is the proteins, are present in both the cellulosic and resinic parts of coal either the solvents used have not been the right ones or else the protein was decomposed and scattered since the resinic extracts show no protein content.

Thus it is seen that much of the work with solvents upon coal has led to the very generally accepted theory that the organic con-



stituents of coal fall into two classes, the cellulosic and the resinic. The resinic type is that claimed to be present in the extractive matter, while the cellulosic is found in the residue. This general hypothesis has been substantiated by numerous investigators using various solvents. A very plausible interpretation of this theory may be stated in a slightly different way, which may give a new aspect to the subject. According to various work done on the constitution of coal it may be said that there are two kinds of resins in coal, the original gum or fossil resins of the plants, and a degradation resin product of cellulose or the cellulosic resins. The extractive matter from coal generally termed "resinic" may then be thought of as containing both cellulosic resins and plant resins principally the former, while the cellulosic "residue" consists of true cellulose plus cellulosic degradation products. Thiessen (28) in his microscopical study of coal, bears out this view in the discovery of more truly plant resins in the "attrital" material, and the cellulosic resin or "anthraxylon" material which he claims has passed through a hydrogell stage. The cellulosic resins may be thought of as forming the large part of the bonding material for coke, while the plant resins yield the paraffins and tar. Solvents used so far have in general extracted the resins as a class without making any selective distinction between the types. Whether the action of selenium oxychloride would throw any light on this question was doubtful, but at least some action dividing the coal into an extract and a residue were expected.

### 3. The Purpose of the Present Investigation:

The purpose of this investigation was primarily to study the action of Selenium oxychloride on coal, in particular, its action as





a solvent. The problem is a new one in so far as a study of the literature shows. Not a great deal is known about the action of selenium oxychloride as it is one of the newer compounds, and as the reagent is not plentiful on the market. Literature on selenium oxychloride is limited to a few brief articles and to one brief mention of its action on coal. The work referred to is by Prof. V. Lenher (27) who is perhaps the best authority on selenium oxychloride in America. He reports the following results from treatment of various types of coal with the reagent:

With natural coals the bitumen is extracted leaving a carbonaceous residue. Anthracite coal containing little volatile matter shows little action. Semi-anthracites lose considerable amounts of extractive matter. Illinois, Ohio, cannel, and bituminous coals from Pennsylvania and Virginia lose a large amount of extractive matter. The insoluble residue was found to contain selenium and chlorine. With powdered coals selenium oxychloride reacts evolving heat. Thoroughly ignited coke loses nothing.

With these points in mind and remembering the extremely reactive nature of the solvent and the difficulty with which it may be handled the present work was begun. It was decided to confine the investigation to one representative coal. With no precedent as a basis upon which to begin work the following general points were laid down as a basis upon which to conduct the investigation:

- 1- To ascertain the nature of selenium oxychloride for the purpose of classifying it as a solvent or a reagent.
- 2- To determine the most efficient method of handling it in connection with coal solvent work.
- 3- To observe the effect of selenium oxychloride upon coal both



physically and chemically.

4- To observe the effect of the solvent upon any substances known to be in coal, or formed from coal by such processes as destructive distillation and carbonization.

5- To note any oxidation effect.

6- To attempt to separate unchanged one or more fundamental parts of coal.

7- To distinguish if possible between the various types of resinic material in coal.

## II. Experimental, Part I.

### 1. The Nature of Selenium oxychloride:

Only very pure selenium oxychloride can be used in solvent work. The solvent hydrolyzes very easily and must be protected from moisture and even from long exposure to the air of the laboratory. There are three methods used in manufacturing the solvent, but without special apparatus it is very difficult to turn out a pure product and protect it from hydrolysis while making. Hydrolysis throws out the red, amorphous form of selenium and converts the oxychloride into the acid. Because of the expense connected with the purchase of the reagent careful use of rather small quantities was necessary. It was found however, that accurate results may be obtained from use of small portions of the solvent provided a reasonable proportion of coal is taken. Surplus of selenium oxychloride present during extraction does not materially change the results of its action on a given quantity of coal.

The highly reactive nature of selenium oxychloride is established by a study of its chemical and physical properties, and there





is little need of confirmatory evidence through use of it on coal to place it in the list of strongly reactive chemicals. The reagent is a liquid, slightly yellow in color as ordinarily prepared. Its boiling point is variously given at from 175'-179'C. The reagent dissolves with ease such non-metals as members of the sulfur family. There is an explosion with such substances as white phosphorous, potassium, turpentine, and sometimes with unsaturated hydrocarbons. The halogens are dissolved. carbon in form of graphite, charcoal, activated charcoal and the diamond are not attacked in the cold. Practically all metals are attacked, more rapidly at higher temperatures, to give the chloride of the metal and red-brown monochloride of selenium. Carbonates of Na, K, Sr, Zr, react with liberation of  $\text{CO}_2$ . Other carbonates are attacked slowly. Natural asphalts, resins, and bitumen dissolve with ease in the cold when they are of unsaturated character. Gums, resins, paints, lacquer, celluloid and glues dissolve. Insoluble phenolic condensation products such as bakelite dissolve readily. Vegetable and fish oils form a rubber like mass. Protein materials dissolve more readily when heated. With carbohydrates, cellulose is not attacked. Starch and sugars are decomposed when heated. All forms of rubber react chemically in the cold. The chemical character of the rubber is changed. The more common sulfides react. Most oxidizing agents dissolve.

The action of selenium oxychloride upon the hydrocarbons is of special interest. Saturated aliphatics such as decane, pentane, and hexane are non miscible, the hydrocarbon floats on top of the reagent. The paraffins are very slowly attacked at high temperatures. Unsaturated hydrocarbons unite directly. The heavier paraffins such as vaseline and paraffin float on top of the reagent, but when heated to 150'-160'C. the two become miscible until cool. Aromatic



hydrocarbons such as benzene, toluene and xylene make perfect solutions. It has long been accepted that there was no reaction with these hydrocarbons, and it is doubtful if any action does take place under thirty hours. This will be considered more at length later in the text. Benzene and toluene from physical mixtures which can be separated by physical means such as fractional distillation. The complete recovery of the hydrocarbon can also be accomplished by hydrolysis of the selenium oxychloride with water. The separation of hydrocarbons may be made by employing selenium oxychloride. Saturated paraffins may be separated from unsaturated, and aliphatic from aromatic. The aromatic form a solution while the lighter aliphatic rises to the top forming an immiscible layer.

Chloroform, carbon tetrachloride, carbon disulfide and benzene are good solvents for selenium oxychloride. The same care must be taken in the laboratory with this reagent as with any other highly corrosive liquid. Vapors inhaled hydrolyze with the mucous membrane of the throat and nose forming hydrochloric acid with an irritating result. Phosgene is readily formed by decomposition of selenium oxychloride. This poisonous gas together with moisture are the two main things to guard against. As has been stated, water, alcohol, and moist air of the laboratory will hydrolyze the reagent. Utmost precautions must be taken to have all apparatus and materials clean and absolutely dry. Since selenium oxychloride is acid in nature moisture forms selenous acid and gives off HCL fumes with the attendant precipitation of red selenium. Cork stoppers are as impossible of use as are rubber. They are slowly dissolved by the fumes of the reagent. Dry ether is miscible in all proportions. Kerosene and gasoline are largely immiscible in the cold. The kerosene gradually becomes discolored.





## 2. The Type of Coal Used:

For this investigation a high grade, low sulfur Illinois Bituminous coal was used. The coal is a fairly good coking coal from Franklin county going under the trade name of Makitan, and is very representative of the better class of Illinois coals. A large supply of fresh coal was obtained and stored in size large enough to prevent rapid weathering. A portion for analysis was ground to 60 mesh after air drying, and the following complete proximate and ultimate analysis made upon the Air dry basis. Percentages were computed to other bases as indicated.

Analysis for:	As Rec'd.	Air dry.	Dry.	Combustible.
Air dry loss	3.05			
Moisture	6.28	3.33	-	-
Volatile matter	33.21	34.26	35.42	39.08
Ash	8.74	9.02	9.33	-
Fixed Carbon	51.77	53.39	55.25	60.92
Total Carbon	69.93	72.17	74.62	82.40
Sulfur	0.998	1.02	1.054	
Nitrogen	1.45	1.50	1.55	
Oxygen	8.011	8.24	8.55	
Hydrogen	4.601	4.72	4.90	
B.T.U.	12,451	12,843	13,280	
Unit coal	14,810			

The analytical work was carried out along the lines and methods used by the Division of Applied Chemistry in coal, gas, oil and other fuel analysis. The Total Carbon was determined in a Parr Total Carbon apparatus. The Sulfur by the Parr standard sodium peroxide method. The Nitrogen by the Kjeldahl-Gunning method. The Hydrogen





and Oxygen were calculated by use of Dulong's formula excluding moisture according to the University of Illinois method. This method has shown exactness better even than the ordinary combustion methods. The calorific values were determined in the Parr Oxygen and the Parr Standard calorimeters, several check runs being made in each. The unit coal value was calculated according to the Parr formula. These methods were used throughout the investigation whenever analysis was required. Any deviation from the standard methods will be pointed out when used.

### 3. The Use of a Neutral Solvent with Selenium Oxychloride:

#### 1'. Selection of the Neutral solvent:

In some lines of work with selenium oxychloride, such as the separation of metals, a diluting agent like sulphuric acid is used to advantage to lessen the powerful action of the selenium oxychloride. This method of handling the reagent was first applied to the present investigation on coal. An attempt was therefore made to find a satisfactory neutral solvent to use as a dilutant for selenium oxychloride. Such a substance must be a liquid and must have no solvent action itself upon the coal, nor react in any way with the selenium oxychloride. If such a substance could be found it was intended to use it with the selenium oxychloride in various concentrations thus obtaining selective solvent action upon the coal. At the beginning of the investigation it was thought that pure selenium oxychloride itself alone would have too great an effect upon the coal, probably dissolving most of the coal and preventing any separation of extract and residue.

After studying the action of selenium oxychloride with various substances it was found that the aromatic hydrocarbons benzene,



toluene and xylene answered the requirements most fully. They are miscible in all proportions with the reagent with which they are not supposed to react. Two extractions of fresh coal were made with each of these hydrocarbons to determine which had the least solvent action upon the coal. Five grams of coal, after being dried at 105° for an hour, were extracted with 70 cc. of the hydrocarbon in a Soxhlet extractor for seven hours at the boiling temperature of the hydrocarbon. The temperature of extraction varied of course with the hydrocarbon used, and the time allowed was sufficient to allow for complete extraction since maximum results were desired. Upon completion of the extraction period the coal residue in the cone was washed for two hours with 95% ethyl alcohol to remove the hydrocarbon, and then with ethyl ether to wash the residue free of alcohol and leave the mass in a condition ready for quick and complete drying. The hydrocarbon extract solution together with the alcohol-ether washings was poured into a small distilling flask and all but fifteen cubic centimeters of the liquid mixture distilled off. The remaining liquid containing the extract was transferred to a small weighed beaker and evaporated to dryness on an electric hot plate. The dry extract material from all three hydrocarbons was dark brown and rather gummy. After drying the extract was cooled and weighed. The gain in weight of each weighed beaker indicated the amount of extraction from five grams of coal by the hydrocarbon solvent used. Percentage extraction was calculated from the weight of the extract. The residues were removed from the cones and dried, together with the cones, in an electric drying oven in a stream of dry air. When dry and in equilibrium with the atmosphere of the laboratory the residues were cooled and weighed. Percentage extraction was calculated from





the weights of the residue. In all cases the percentage extraction as calculated from the extract was much higher than that calculated from the dry residue. There is a possibility that the extracts were not separated thoroughly from the solvent. Extraction as calculated from the residue was taken as more nearly correct. Results obtained here closely check with investigation carried out elsewhere along the same lines. Table I shows the average results from this test.

Table I.

Solvent	% Extraction (cal c. from extract)	% Extraction (cal c. from residue)
Benzene	5.41	2.62
Toluene	3.30	1.77
Xylene	1.22	0.25

From these results it was concluded that xylene was the best neutral solvent to use with selenium oxychloride. The xylene used was a mixture of the o,m, and p xylenes. The clear distillates of the xylene, alcohol and ether were evaporated and no trace of coal extract found in them.

## 2'. Apparatus and Procedure:

A series of ten extraction runs were made using a ten percent solution of selenium oxychloride and xylene, and varying the time of extraction and the temperature. The apparatus used is shown in Figure I. Ten grams of air dried coal were dried at 105°C. for an hour in an electric drying oven. The coal to be extracted was then transferred rapidly from the drying oven to the extraction flask (h). 100 cc. of the solvent solution (90 cc. of xylene to 10 cc. selenium oxychloride) were added to the flask. The extraction flask was a 250 cc. wide mouth pyrex flask with flat bottom, three inches in height in



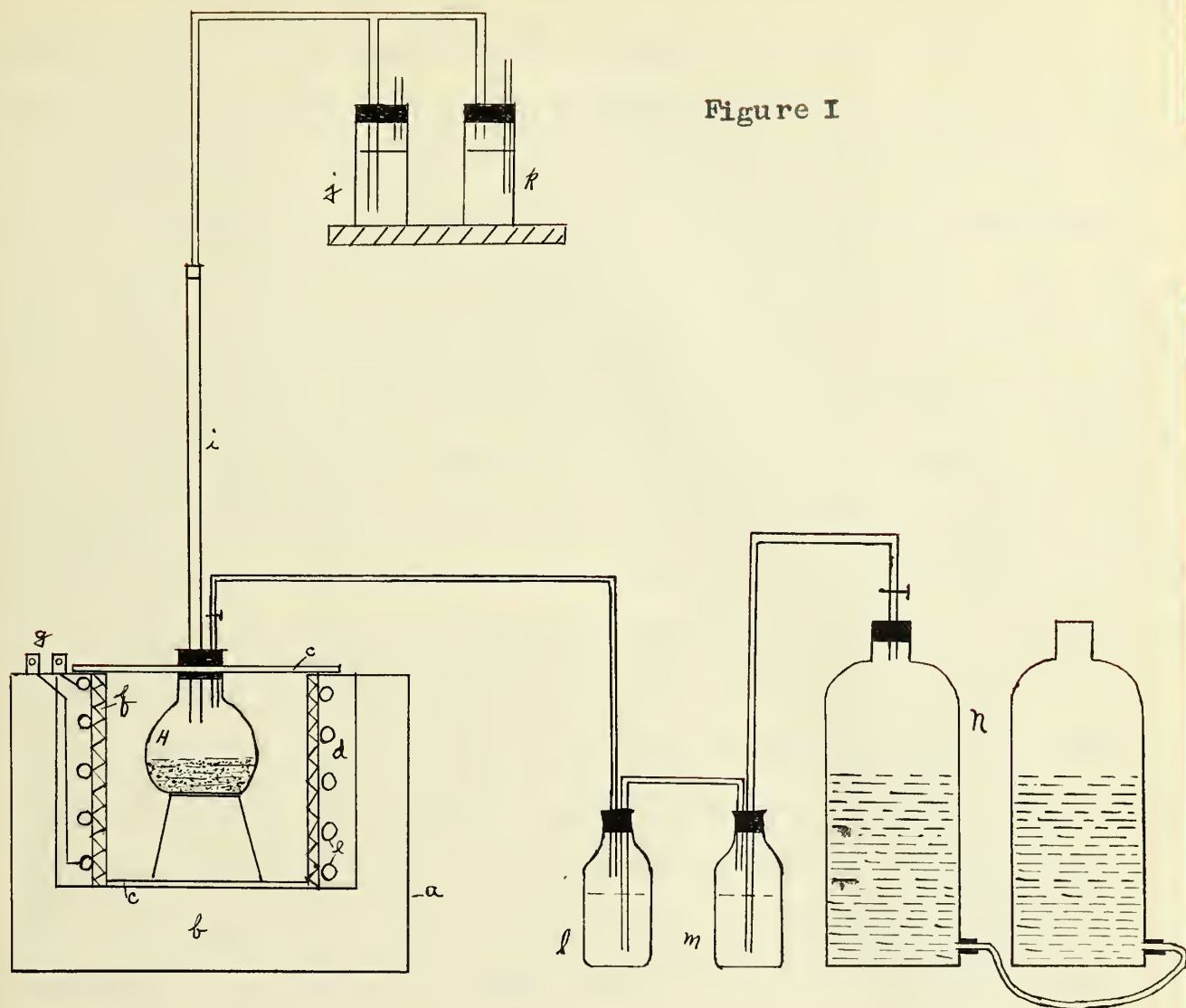
the body and measuring three and one-fourth inches in diameter at the widest point. Cork stoppers were used and the flask connected to an air reflux condenser (i) consisting of a glass tube three feet long and one-half inch in diameter. All connections were sealed with a mixture of litharge and glycerine. Dry nitrogen free from oxygen, obtained by passing the gas through the drying train (l,m,) was passed into the extraction flask from the nitrogen reservoir (n) at constant pressure for a time to displace all air. During extraction a slow stream of nitrogen was passed thro the apparatus escaping thro the air condenser and out the sulfuric acid trap (j). Contraction in the flask was relieved by automatic taking in of air thro the alkaline pyrogallol trap (k) which removed the oxygen. The extraction flask was held upright in an electric resistance furnace shown in detail in Figure I, and was shaken occasionally during the extraction. Temperature measurement was taken in this series of runs with an ordinary mercury thermometer, and heat control was obtained by use of resistance coils shown in a later figure. The first eight runs were made at room temperature and required no use of furnace. Runs 9 and 10 were made at 100°C. the flask being cooled down to room temperature in an atmosphere of nitrogen after completing the run. The time of extraction of the eight runs made at room temperature (20°C) was varied from five hours to 137 hours. The two runs at 100°C were of five hours duration. Very little if any heat was given off by action of the solvent mixture during the extractions at room temperature. During extraction the mixture in the flask was reddish-brown in color and showed green fluorescence.

After extraction the contents of the flask were poured out into a large paper filter and the flask rinsed out with xylene. The residue on filter was well washed with xylene and the extract solution





Figure I



a- galvanized iron casing

b- asbestos-magnesia insulation

c- asbestos board

d- alundum cement

e- chromel wire coil

f- iron cylinder

g- binding posts

h- extraction flask

i- air condenser tube

j- sulphuric acid trap

k- alkaline pyrogallol trap

l-  $H_2SO_4$  drying bottle

m- alkaline pyrogallol bottle

n- nitrogen reservoir





together with the xylene washings caught in a large Erlenmeyer flask. The color of this extract solution after filtering was red-brown, much darker than the original solvent mixture, and had a rather oily appearance. The color of this solution deepened according to the length of time and the temperature of the extraction. The residue was next washed with small portions of ether to remove the xylene. This washing was continued until the wash liquid was fairly colorless. These ether washings were kept separate from the extract solution. The residue at this stage was black with the general appearance of wet powdered coal. It was now transferred while still wet with ether to a 200 cc. Erlenmeyer flask. Nearly all of the residue can be transferred to the flask, but even with the greatest care some is lost on the filter and during the repeated washings process. This flask containing the residue was placed in the electric furnace and connected to the nitrogen drying train. Outlet to the flask was secured by means of a small glass tube instead of the reflux air condenser. The open end of this tube passed into a sulfuric acid trap to protect the drying flask from moisture. Dry nitrogen was passed through this drying flask over the residue, which was dried for from 5 to 12 hours at a temperature of from 200°-280°C. Ether fumes were bubbled off through the sulfuric acid trap together with the escaping nitrogen. The flask was next cooled down in this atmosphere of nitrogen and opened, and the residue now quite dry and powdery was transferred immediately to a weighed sample tube and sealed. The coal residue thus cleaned and dried was black and shiny, much like the original coal in appearance. They had only a trace of odor of ether about them.



### 3'. Examination of Products and Analysis:

The sealed tubes containing the residues were weighed and in each case a gain in weight, instead of a loss, was found. Because of this gain in weight it was not possible to tell whether there was any loss due to solvent action of the reagent upon the coal. Such a gain in weight indicates that the residue in all probability was not washed free of the solvents, and that the selenium oxychloride attacked or decomposed some part of the coal which added on selenium and thus added weight to the residue. There is little doubt but that there is some form of selenium, either red or gray, present in the residues as thus prepared. The great variance of gain in the ten runs is due to the extraction and to the chemical action of the reagent resulting in the decomposition of selenium oxychloride to deposit selenium in the residues. In Table II. is given the data on these ten runs showing the gain in weight of the residues for the given time and temperature of extraction.

Table II.

Run	Temperature	Time	Drying	Gain	Percent gain
1	20 'C.	5 hrs.	5 hrs.	.5064 gm.	5.06
2	"	"	6	.6999	6.99
3	"	28	8	.4878	4.87
4	"	30	12	.4190	4.19
5	"	91	12	.8886	8.88
6	"	69	11	.8200	8.20
7	"	116	11	.4540	4.54
8	"	137	12	.7802	7.80
9	100	5	12	.8868	8.86
10	100	5	10	.4561	4.56

Residue #1 was taken from the sealed tube in which it had been kept and reweighed. A gain of P.PQXY gm. was found probably due to oxidation and absorption of moisture. The residue was placed in an extraction cone and extracted in a soxhlet apparatus for three and one-half hours with 70 cc. of ether. The ether was only slightly





colored at the end of the extraction. After drying in an atmosphere of nitrogen for six hours at 200 °C. the residue was found to have lost 0.2589 gm. or 2.46%. The same residue was then returned to the soxhlet apparatus and extracted with different portions of carbon disulphide for several hours. The carbon disulphide turned light brown very quickly. Red and brown crystals of selenium were extracted from the residue by the carbon disulphide and were thrown out of solution by the addition of ether and cooling.

The ten residues from the xylene-selenium oxychloride extractions were analyzed for moisture, volatile matter, ash, fixed carbon, total carbon and sulfur. The results are shown in Table III. Percentages are tabulated upon both the air dry and the ash free-moisture free bases, and are compared by a column of difference with the corresponding results on the original coal.

The extract solutions from the xylene-selenium oxychloride extractions were examined as follows. The extract solution was distilled at reduced pressure from a Claussen pressure distilling flask. A clear yellow distillate came over between 20° and 70°C. This distillate rapidly turned light amber in color and showed a yellow-green fluorescence. It smelled strongly of selenium oxychloride and white fumes were thrown off during most of the distillation. Examination of small portions of this distillate by the use of water, alcohol, ether, HCl, ammonium hydroxide, potassium hydroxide together with various distillations and fractionations showed the distillate to be composed of xylene and selenium oxychloride together with a small amount of selenious acid. The color was imparted to the distillate by traces of red selenium and a gummy compound of xylene in union with decomposition products of selenium oxychloride.



Table III

No.	H <sub>2</sub> O	DIFF.	V.M.	DIFF.	7.C.	DIFF.	ASH	DIFF.	T.C.	DIFF.	S.	DIFF.	V.M.	DIFF.	PURE	7.C.	DIFF.	PURE	T.C.
Coal	3.33		24.26		53.39		9.02		72.17		1.02		39.08		60.92		82.4		
1	9.79	+6.46	26.17	-8.07	56.34	+2.95	7.73	-1.29	62.6	-9.6	9.33	+8.31	31.71	-7.37	68.25	+7.33	76.1	-6.3	
2	.79	-2.54	31.51	-2.15	59.80	+6.41	7.90	-1.12	64.0	-8.2	5.19	+4.07	34.50	-4.58	65.50	+4.58	70.0	-12.4	
3	.12	-3.21	37.61	+3.35	53.16	-.23	9.11	+1.09	63.8	-8.4	3.96	+2.94	41.43	+2.35	58.60	-2.32	69.2	-13.2	
4	.12	-3.21	34.68	+.42	56.19	+2.18	9.01	-.01	64.1	-8.1	4.25	+3.23	38.16	-.92	62.0	+1.08	70.5	-11.9	
5	1.34	-1.99	29.56	-4.70	60.85	+7.46	8.25	-.79	60.7	-11.5	3.34	+2.32	32.69	-6.39	62.5	+1.58	67.2	-15.2	
6	.65	-2.68	36.80	-2.54	53.39	0.0	9.16	+1.14	62.2	-10.0	3.05	+2.03	41.80	+1.72	69.2	+8.28	69.0	-13.4	
7	.07	-3.26	29.70	-4.56	61.43	+8.04	8.80	-.22	63.6	-8.6	1.46	+0.44	32.59	-6.49	67.25	+6.33	69.7	-13.7	
8	.28	-3.05	30.60	-3.66	60.44	+7.05	8.18	-.34	61.6	-10.6	3.74	+2.72	33.61	-5.47	65.25	+4.33	69.8	-14.6	
9	.35	-2.98	39.05	+4.79	51.92	-1.47	8.68	-.34	61.5	-10.7	4.23	+2.21	43.00	+3.92	57.0	-3.92	69.7	-14.7	
10	.97	-2.36	38.57	+4.31	51.01	-2.20	9.07	+0.05	60.7	-10.5	2.45	+1.43	43.00	+3.92	56.75	-4.17	69.6	-14.8	





There remained in the Claussen flask a very dark, red-brown mass which appeared to be a mixture. Decantation, hydrolysis and filtering finally separated the mass into two parts. The largest portion of the mass was composed of a brown, gummy substance consisting of the extracted material of the coal in combination with xylene and decomposition products of selenium oxychloride. Much red amorphous selenium was scattered throughout this gummy substance. The other part of the residual mass consisted of gray selenium formed by the heating of the precipitated red selenium thrown out during the distillation process. Any extract material from the coal is combined in this brown-red, gummy syrup, but a separation of the extract from the addition compound holding it was found to be impossible. The material is very thick and viscous with the same yellow-green fluorescence that colored the xylene distillate. Upon standing the mixture, for such it must be called, tends to harden. When heated the mass gives off white fumes and the odor of rotten radishes characteristic of selenium compounds when decomposed by heat. Heating does not seem to evaporate the substance to any marked degree.

During examination of a large portion of extract solution from one of the ten runs the solution was shaken with a large quantity of water and, quite by accident, allowed to stand about thirty minutes before separating in a separatory funnel. A heavy cloud of white crystals settled out in the funnel between the water layer and the oily extract-xylene layer on top. The water and the crop of white crystals were drawn off and the extract solution repeatedly washed with water until no more of the white substance could be obtained. The crystals proved to be very pure. They were subjected to physical and chemical tests including qualitative organic analysis and





were found to be pure xylene selenic acid, formed by action of the selenium oxychloride upon the diluting xylene in the solvent mixture.

The ether washings of the residues were examined and were found to contain ether, xylene, selenious acid, selenium and the same xylene-resiniceselenium mixture identified in the extract solutions.

After identification of a compound due to chemical action between selenium oxychloride and xylene a test was made upon the reagent to learn more of its action upon the aromatic hydrocarbons. Equal portions of benzene, toluene and xylene in separate test tubes were mixed with the same amount of pure selenium oxychloride and the tubes sealed. After fifteen hours the benzene showed no change, the toluene had turned a deep wine color, and the xylene had become entirely opaque being a brownish-black color. After three days the toluene and xylene solutions were both quite black with a green fluorescence while the benzene solution had turned a faint yellow. At the end of five days the three tubes were hydrolyzed with water. The benzene was the only hydrocarbon of the three which separated out on top of the water in anything like its pure form. The other two tubes showed heavy precipitations of red selenium and other signs of decomposition.

#### 4'. Carbonization of Residues:

In order to obtain further indications as to the action of this mixed solvent upon coal, a carbonization run was made upon a mixed sample of residue from the ten runs. The products of carbonization and analysis of the gases yielded were the principle factors under observation. The apparatus for carbonization and the methods of analysis used were identical with those explained in detail later on in the text, so no further reference will be made to them at this



point. The data and results of the run are listed in Table IV. There was no sign of tar in the tar trap or in the retort. Red selenium was scattered throughout all the apparatus even in the gas holder. The gas generated or yielded by the residue had a very acrid odor causing extreme irritation to the nose and eyes. When passed over lead acetate paper it turned the paper black. Selenium in the residue combined with hydrogen of the coal residue to form hydrogen selenide. This gas decomposes in part to give red selenium found throughout the apparatus. To free the gas from the poisonous hydrogen selenide so that it might better be analyzed, it was passed through three tubes of lead acetate. The gas free of hydrogen selenide, which would have caused an error in the percentage of carbon dioxide, was then analyzed in a U. of I. Modified Orsat apparatus as will be explained later.

### III. Results, Part I.

#### 1. The Nature of Selenium oxychloride:

It is evident that selenium oxychloride must be regarded as a very highly active reagent. It is not a good solvent in that it is impossible to secure a satisfactory separation of extract, residue and the reagent. Recovery of the reagent by hydrolysis, with the liberation of any extracted material, is not possible in coal work as it is in the separation of aromatic hydrocarbons and selenium oxychloride, because of chemical reaction between the reagent and coal. As prepared selenium oxychloride is very expensive, too much so to allow of much work with it commercially on coal. Selenium is however very plentiful, and should there be a demand for commercial use of the reagent, no doubt a cheaper and easier process of manufacture could be perfected.





Table IV.

Weight residue coked 30.0 gm. from extractions 2, 4, 8, and 10.  
 residue 22.79 = 75.96%  
 tar 0.00

Type of residue: No sign of coke, powdered like original.

Combined data on run:

Time	Temperature	Gas Volume	Remarks
0 '00"	Room	0	
15	70	100	
35	190	250	Moisture on retort.
45	265	290	
55	300	400	
1 00	330	575	
1 15	390	800	
2 00	500	1800	
3 05	555	2900	
3 15	575	3040	
4 00	590	3400	
4 30	595	3600	
4 55	605	3750	
5 45	615	3950	
6 20	625	4100	

Gas data:

Temperature (maximum) 625°C.

Time in hours 6.33

Total gas 4100 cc. including  $H_2Se$

Gas analysis:	I	II	Average	Nitrogen free
$CO_2$	8.0%	7.9%	7.9%	10.7 %
$O_2$	5.8	6.1	5.9	8.1
$C_2H_4$	0.0	0.0	0.0	9.0
$C_6H_6$	0.0	0.0	0.0	0.0
$H_2$	27.2	24.9	26.0	35.7
$CO$	7.0	7.0	7.0	9.5
$CH_4$	24.8	-	24.8	34.5
$C_2H_6$	1.2	-	1.2	1.5
$N_2$	26.0	-	27.2	0.0

## 2. The Action of Xylene-Selenium oxychloride Mixture on Coal:

From the results shown in Table II. it is not possible to draw any conclusions as to comparative amounts of extraction due to the length of the extraction period or to the temperature of extraction. There is undoubtedly more extraction of the coal at the higher temperatures and during the runs of greatest duration, but the chemical action of the reagent upon the coal and the xylene varies to such an extent that no definite quantitative results are possible. The



deepening in color of the extract solutions from the runs of greatest length would seem to point to more extraction or to greater chemical action.

Extraction of residues from the mixed solvent extractions shows the presence in the residues as prepared of selenium and also quite a little extractible matter which may belong to the coal or may have been added to the residue through the formation of some xylene compound.

Analysis of residues gives only comparative results at best. The volatile determinations left no coke buttons whereas the original coal did. This is an indication of the loss of coking property through extraction. The volatile matter while burning off gave evidence of chlorine and selenium in the residue. Volatile matter air dry shows a loss in six of the ten runs. The net result for the ten runs shows an average loss of 1.33%. On the pure coal basis the volatile matter shows an average loss of 2.22% for the ten runs.

The ash of the original coal was light gray. All ash from these runs except run 1 and 2 showed presence of selenium by their brown-red color. Seven of the ten runs show a loss in ash on the air dry basis for an average of 0.50%.

Moistures on runs 2-10 inclusive show an average loss of 2.81%. This loss in moisture is explained by the treatment of the residues which excluded absorption of moisture from the air. The moisture figures are however not important and may be ignored. The loss in ash is so small as to be within experimental error. Provided the selenium oxychloride did not attack some inorganic constituent of the coal it is safe to assume that the ash remains the same after treatment as in the original coal.

Fixed carbon air dry shows a gain in six of the ten runs





corresponding of course to the volatile loss. For the ten runs the average gain equals 4.43%. For a check it may be seen that the average gain in fixed carbon approximately equals the sum of the average loss in moisture, volatile matter and ash. The Fixed carbon on pure coal basis shows an average net gain of 1.31%.

The total carbon air dry shows a loss in all ten runs for an average of 9.62%. This verifies the loss in volatile matter above. It seems that the small amount of selenium oxychloride present in the solvent mixture ( ten percent ) was able to remove carbon in the form of unsaturated compounds, and it is safe to assume that there was solvent action to the extent of removing some unsaturated hydrocarbons and resinic material. On the pure coal basis the total carbon shows a loss in all ten runs for an average of 13.02%. It is interesting to note that the amount of loss in total carbon on this basis increases with the increased length of the extraction time and with the rise of temperature.

Sulfur air dry shows ten gains for an average of 2.37% excepting #1 which is abnormally high. Sulfur was determined here direct from the total carbon residues and hence any selenium present will be determined with the sulfur. This is an added proof of the presence of selenium in the residues.

From the standpoint of extracted material the use of xylene to dilute selenium oxychloride is a failure since it is impossible to isolate any extract and because there is more chemical reaction between the xylene and the reagent than solvent action upon the coal. Most of the xylene can be recovered pure, but the selenium oxychloride decomposes with the treatment. The red amorphous form of selenium is present everywhere. It is very probable that some chemical





action has taken place between part of the xylene and the selenium oxychloride. The dark, heavy syrup substance is composed of red selenium together with any xylene compound formed and any tar or resinic material extracted from the coal. From the nature of the material it seems very probable that some resinic material has been dissolved out of the coal, but this can not be isolated and identified as such. The hard, gray substance formed upon heating the extract is the gray crystalline form of selenium which is formed from heating the red selenium. The red amorphous selenium is thrown out from selenium oxychloride every time hydrolysis or chemical reaction takes place. Any subsequent heating of this form over 150°C will result in the formation of the gray selenium which is not soluble in carbon disulphide as is the red variety.

Selenium oxychloride probably forms some new compounds either with the resinic material of the coal, the xylene, or both. Unsaturated hydrocarbons of the coal might be attacked, but there is no way of telling what the resulting compound would be. Any chemical reaction with aromatic hydrocarbons will result from action upon xylene since there are no aromatic hydrocarbons in coal as such.

### 3. The Carbonization of Residues:

Very interesting results were obtained from the data on the carbonization run made on the residue from the xylene-selenium oxychloride solvent, and from the gas analysis of this same run. There are no unsaturated hydrocarbons or benzene in the gas as analyzed. Benzene in coal is formed from unsaturated hydrocarbons. The selenium oxychloride here evidently removed the unsaturated hydrocarbons from the coal, thus removing both unsaturated aliphatic and saturated aromatics from the gas. The carbon dioxide in Table IV. may



be slightly high due to the fact that any hydrogen selenide not removed by the lead acetate train will be absorbed by the KOH along with the carbon dioxide. The hydrogen also may be low due to the loss of hydrogen which united with selenium to form the selenide. The most important results of the coking run is the absence of tar among the products, and the absence of the hydrocarbons from the gas, as pointed out above.

#### IV. Conclusions, Part I.

No quantitative extraction of coal is possible with selenium oxychloride as a solvent because of chemical action and deposition of selenium which is difficult to remove. The presence of xylene increases the amount of chemical action and thus the amount of selenium left in the residue and extract. When xylene is used to dilute the reagent there is more chemical action at higher temperatures and in extractions covering the most time. Most of the xylene can be recovered, but its presence leads to greater decomposition of the reagent. The most careful and rapid treatment is necessary to give a minimum amount of the red selenium which upon heating turns to the gray metallic variety.

Xylene or any other neutralizing agent will not work with selenium oxychloride in coal research due to chemical action and the complication of products. While not successful as a final method, the use of xylene will give good preliminary results and indications of what may be expected from the use of pure selenium oxychloride on coal. This shows that the most nearly perfect neutral solvents are not fitted for use as a dilutant. If any application of selenium oxychloride is to be made it must be in the concentrated form which will eliminate confusing side reactions.





Selenium oxychloride reacts chemically with some part of the coal conglomerate. Chlorination with substitution of red selenium results. It may be possible to free the residue from selenium so as to obtain a pure residue for analysis. The extracted material, which is probably resinic in nature, enters into chemical combination with the reagent and no separation is possible. New compounds probably of the additive type are formed.

Selenium oxychloride unites with xylene to form such compounds as xylene selenic acid.

Selenium and chlorine are both present in residues from this method of extraction.

Analysis of the residues shows very little action upon the ash of coal, but a loss of carbon content both volatile and fixed.

Selenium oxychloride destroys the coking property of coal and extracts the tar or tar forming constituents of the coal as shown by the direct carbonization run. The extracted material is probably composed of unsaturated hydrocarbons and resinic material.

Hydrogen selenide must be removed from the coke gas before analysis. More efficient treatment of residues may give a residue free from selenium and thus eliminate the  $H_2Se$  from the resulting gas.

## V. Experimental, Part II.

### 1. The Effect of the Tar and Volatile Content of Coal Upon the Resulting Action of Selenium oxychloride:

It would seem from the above results that the higher the percentage of volatile matter and the more tar or tar forming material in a coal the greater will be the amount of extraction with selenium oxychloride. If this is true coke, with no tar and very little



volatile content, should show no extraction, and a partially coked coal residue should show only a small amount of extraction. To test these conclusions the following extractions were made using pure concentrated selenium oxychloride.

One to three gram samples of coke ground to 60 mesh were shaken together with a portion of the reagent in a small Erlenmeyer flask for from fifteen to thirty minutes. The flask was warmed a few times. The contents of the flask filtered easily and there was no sign of any resinic or gummy material mixed with the selenium oxychloride which filtered through. To the filtrate, rather black in color, was added sufficient water to hydrolyze the selenium oxychloride. Red selenium separated out but upon refiltering this was the only substance left upon the filter. The residue remained black and in the same condition as before extraction. Washing with water removed all the reagent but resulted in throwing out much selenium which remained in the residue.

A fresh sample of air dried coal was kept in a small stoppered flask with selenium oxychloride for one week. At the end of this extraction period it was found impossible to filter off the reagent or any extract solution. The whole mass was brown-black in color, with the consistency of a heavy paste. Water was added and the mixture stirred. When filtered the filtrate was clear water only. This showed that the extract had undergone such chemical reaction as to produce a gummy substance insoluble in water. Alcohol dissolved the substance enough to allow filtering. The filtrate was chocolate brown in color. The residue after being treated with alcohol was black with a slight brownish tinge. It showed traces of selenium.

A coal sample was secured which had been ground to 60 mesh, air dried, and partially coked up to 500°C so that practically all the





tar had been distilled out. This sample was treated with the reagent for various lengths of time. The result upon filtering was much the same as with coke. The mixture filtered rapidly and the filtrate showed no signs of resinic extract obtained from fresh coal.

A sample of fresh coal was mixed with the reagent for a half hour and the mixture then filtered. Filtration was nearly impossible due to the thickness and gummy nature of the solution.

## 2. Efficient Methods of Handling Selenium oxychloride:

One of the most convenient and useful pieces of apparatus made use of in solvent work, the soxhlet extractor, was first tried out.

Air dry coal from which all traces of moisture were further removed by heating to  $105^{\circ}\text{C}$ . was used in the extraction cone, and a sufficient amount of selenium oxychloride was taken to allow proper operation of the apparatus. Cork stoppers were used since they showed less attack from the reagent than rubber. It became evident almost at once upon starting the extraction that this method would be impossible to use. The reagent attacked the corks at once, dissolving them to a jelly in a few minutes at the temperature developed. The whole of the selenium oxychloride became a dark brown color showing marked decomposition of both reagent and cork. Some of the reagent after refluxing ran down into the extraction cone and that too was dissolved into a pulp in a few minutes.

Another method of refluxing was tried. An ordinary glass tube was attached to a small flask, containing the coal and reagent, to serve as a condenser. Here the results were also negative. The reagent attacked the stoppers and was itself decomposed upon heating. Marked hydrolysis was noted in the tube where the air came in contact with the reagent.





From these attempts it was evident that no heating of the reagent to anything near its boiling point was advisable or possible and also that no refluxing system of extraction could be used.

### 3. Extraction of Coal with Selenium oxychloride:

#### 1'. Apparatus and Procedure:

Bearing in mind the results of the previous tests the following final method was adopted as the most efficient means of treating coal with selenium oxychloride. Twenty-five gram samples of coal were weighed out and dried in an electric drying oven for an hour at 105°C to remove all moisture. When dry each sample of coal was removed rapidly and transferred to a small Erlenmeyer flask (200 cc.) and sufficient selenium oxychloride was poured in to just give an excess above a thin paste. The flasks were stoppered at once with cork stoppers. The coal mass swelled a great deal and much heat was evolved, the flasks becoming too hot to hold. The flasks were shaken and the contents stirred from time to time. Heat was applied by slight warming on an electric hot plate. The total time of extraction varied from thirty to forty minutes. Preliminary trials showed that any attempt to filter at this stage was impossible, so at this point, a small quantity of benzene was added to the flask and the mixture well shaken and stirred. The benzene will not hydrolyze the reagent or extract any of the coal in the presence of selenium oxychloride. The benzene being miscible with the reagent forms a perfect filtering medium and the mixture when poured into a suction filter will filter with ease. A slight suction was maintained throughout the filtering. The contents of the flask were washed out into the filter with small portions of benzene. The filtering became slower, but with repeated washing of the residue with benzene the process was



completed without much loss of time or hydrolysis of selenium oxychloride. The extract solution was black and very viscous. It contained the selenium oxychloride-benzene mixture together with the extracted substance of the coal. Red selenium rapidly separates out in this extract solution. The solution was stoppered and set aside for examination.

The residue on filter was washed with ether until all traces of benzene had been removed and the ether washings became clear. These ether washings were reserved in a separate flask for examination.

The residue was now scraped out onto a large filter paper, powdered with a spatula and allowed to dry partially. The color at this stage was black with a brown tinge attributed to presence of selenium. The residue gave off a strong odor of chemicals. When nearly dry the residue was transferred to a beaker and repeatedly washed by decantation with benzene until the washings filtered clear. This was to insure complete removal of any selenium oxychloride and extract remaining in the residue. Washing in the same manner with ether gave a fairly clean residue which was dried in a large flask in an atmosphere of nitrogen. When dry the residue was put through a 60 mesh screen and then further dried in drying oven for two hours at from 50'-170'C dry nitrogen being passed thro the oven. A residue was thus secured practically free from chemicals, and black and powdery with the same appearance as the original coal. The residue was stoppered in a sample bottle at once to prevent absorption of moisture or oxidation.

After being washed with ether the residue dries very rapidly and thus danger of much oxidation is lessened. No quantitative results may be expected showing percentages of residue and extract





owing to chemical reaction, deposition of selenium and loss of small amounts of residue through repeated washing and filtering. Because of this loss no check runs are possible. The nature of the extract solution is such as to allow of no separation of the extracted coal substance, and this also renders quantitative work impossible. No extraction and filtration process without the use of benzene to aid in filtering will succeed as the filter clogs and the reagent rapidly hydrolyzes from exposure to the air. Rapid manipulation, exclusion of moisture, and keeping the reagent well mixed with benzene while in contact with the residue and exposed to the air are the essential safeguards for effective use of this extremely simple method of extraction.

## 2'. Examination of Products and Analysis:

Very little attention was given to examination of the extract solution. Preliminary tests showed that any separation of the extract material from the coal was impossible because of the chemically changed nature of the material. The extract, probably resinic in nature, enters into combination with the reagent and is thus changed. Selenium is present in fairly large amounts in this extract mass. Removal of this selenium may be effected only by solvents or reagents which at the same time further decompose the extract.

The ether washings of the residue were mixed together and distilled. Most of the ether was recovered pure, leaving a small amount of heavy, black extract material behind. This was added to the extract solution. The extract solution proper contained the extract, selenium oxychloride, and benzene. Filtration, hydrolysis, fractional distillation and other methods failed to isolate the extracted substance. Most of the benzene was recovered fairly pure. The selenium



oxychloride present is decomposed to give primarily selenious acid and red selenium. The selenium can be removed in part by repeated hydrolysis and filtering. Heating the solution or mixture converted a portion of the red selenium to the gray variety, insoluble in anything but concentrated sulfuric acid, which further complicated the investigation. It is certain that there is some form of extracted coal substance present. The thick, gummy, nature of the extract mass, left after the benzene and selenium oxychloride have been removed, shows this fact. The color of the mass is brown-black, but the presence of selenium gives the mass its color and so prevents the determination of the color of the extract. The odor of the extract is that of rotten radishes which characterizes selenium compounds. It tends to decompose with evolution of heavy, brown fumes when heated in the air. Distillation only dries the mixture forming a hard crust like dry clay. The appearance of this mixture is identical with that obtained from the extraction of coal with the xylene dilution solvent. There is one difference. In the former extraction there was present a xylene-selenium oxychloride addition substance, but in the later case the reagent does not seem to react with the benzene in the least.

The residue obtained however was in nearly pure form and from analysis of it and comparison of the analysis with that of the original coal it was thought possible to determine something of the nature of the extract as well as of the residual material. To free the residue as prepared from selenium it was desired to extract the residue with large quantities of carbon disulphide in which the red variety of selenium is soluble. It did not seem probable that this extraction with carbon disulphide would result in the extraction of





any of the coal substance from the residue along with the selenium, but the following test was made to varyify the assumption.

A small amount of residue from a preliminary extraction with selenium oxychloride was analyzed for moisture, ash, volatile matter, fixed carbon, total carbon and sulfur content. No coke buttons were left from the volatile determination, and the presence of selenium and chlorine in the volatile matter was shown by the brilliant sparks and the copper wire test for halogens. Five grams of the same sample of residue were then extracted in a soxhlet apparatus for twelve hours with carbon disulphide to remove the selenium present. At the end of twelve hours the residue was washed free of carbon disulphide with ether and dried at 105°C. Addition of ether to the CS<sub>2</sub> and cooling threw the selenium out of solution. This was filtered off and weighed. From the five grams of residue 0.1198 gm. of red selenium, or 2.39%, were obtained. This test pointed out the practicability of extracting all the residue with carbon disulphide to obtain a purer residue for examination. The small selenium free sample of residue was analyzed for moisture, ash, volatile matter and fixed carbon. The results of these analyses together with that of the original coal and the differences are shown in Table V. This table shows, on the dry and pure coal bases, that the only effect of the CS<sub>2</sub> on the residue is a lowering of the volatile matter by 3.6% through extraction of selenium which appears in the analysis as volatile matter largely. The fixed carbon is correspondingly increased by 3.6%. No other changes in the analysis of importance, together with the fact that evaporation of the ether and carbon disulphide used failed to show any extract material, proved that extraction of the main residue with carbon disulphide does not re-





sult in any loss of coal material. Accordingly the main residue was extracted in a large soxhlet apparatus with two portions of carbon disulphide for three hours which removed the largest part of the selenium present. After washing with ether for an hour the residue was dried as before and sealed up for further examination.

Table V.

Air dry:	Moisture	Volatile	Ash	Fixed C.	Total C.	Sulfur
Coal	3.33	34.26	9.02	53.39	72.17	1.02
Residue	1.67	50.78	9.25	38.30	51.04	2.78
Residue-Se	4.42	46.21	9.06	40.21	-	-
Difference 1-2	-1.66	+16.52	+0.23	-15.09	-21.13	+1.76
Difference 1-3	+1.09	+11.95	+0.04	-13.18	-	-
Dry basis:						
Coal	-	35.42	9.33	55.25	74.62	1.05
Residue	-	51.59	9.39	39.02	51.86	2.82
Residue-Se	-	48.06	9.42	42.52	-	-
Difference 1-2	-	+16.17	+0.06	-16.23	-22.76	+1.77
Difference 1-3	-	+12.64	+0.09	-12.73	-	-
Pure coal basis:						
Coal	-	39.08	-	60.92	80.40	-
Residue	-	57.00	-	43.00	57.30	3.12
Residue-Se	-	53.40	-	46.60	-	-
Difference 1-2	-	+17.92	-	-17.92	-23.10	-
Difference 1-3	-	+14.32	-	-14.32	-	-



The main residue was analyzed on the Air dry basis. The complete analysis is shown in Table VI.

Table VI.

Analysis for:	Air Dry:	Dry:	Combustible:
Moisture	2.17	-	-
Volatile matter	63.90	65.31	70.90
Ash	7.76	7.94	-
Fixed carbon	26.17	26.75	29.10
Total Carbon	54.89	56.09	60.93
Sulfur	0.81	0.84	0.91
Nitrogen	1.50	1.54	1.67
Oxygen	27.73	28.34	30.79
Hydrogen	5.14	5.25	5.70
B.T.U.	9,062.2	9,261.36	
Unit coal	10,136.4		

#### 4. The Effect of Selenium oxychloride Upon the Primary Volatile Products of the Carbonization of Coal.

##### 1'. Outline of Investigation:

When coal is heated in the absence of air, such as during a coking run, chemical reactions occur of a complex nature and new substances are formed in place of the original coal. These new substances are: the solid residue or coke; liquid products in the form of water and tar; and gas. The yield and character of these products will depend upon the type of coal used, the temperature of the carbonization, the time and the pressure. The first or primary volatile products coming off are changed by secondary decomposition if allowed to remain exposed to a sufficiently high temperature, so in the





average high temperature carbonization run it is doubtful whether any of the final products are liberated from the coal as such. Much information as to the constitution and coking properties of coal may be derived from a study of the primary products of carbonization. For this end it is necessary that the products be removed at once, and that the temperature and time of the run be respectively neither too high nor too long.

With these points in mind and with a view to learning more about the type of residual and extract material obtained from coal by the use of selenium oxychloride, and from this data to develop further if possible the ideas of carbonization and the constitution of coal, the following series of tests were made. A study of fresh coal was first made by means of low temperature carbonization runs. The primary volatile matter of the coal was liberated leaving an altered coal substance or residue in the form of a partly coked solid. Particular attention was given to the residue, tar and gas products. More fresh coal was then treated with selenium oxychloride to remove the tar forming material as has been shown, and this extraction residue subjected to the same coking process. The absence of tar and the composition of residue and gas were noted especially, and compared with results obtained from the fresh coal.

The results of this part of the investigation were intended to varyify the preceeding work and to add to this investigation information relative to the amount and character of the primary volatile products and of the coke residue from the carbonization at low temperature, and the effect of selenium oxychloride in modifying all these factors.

Since one of the main products, the tar, is removed by the reagent, the composition of the gas given off up to the point where



the tar begins to distill and that given off after the tar is all distilled over was noted especially. For this reason the temperature of the different carbonization runs were governed by the temperatures at which the tar first showed and that at which it ceased to distil. Through the courtesy of Wade S. Hawthorne the temperatures of the beginning and maximum softening points of the fresh coal were obtained. The Franklin county coal used throughout this investigation begins to soften at 374°C. and reaches its maximum softened state at 406°C. From this data it is safe to assume that the tar begins to distill from the coal around 375°C.

## 2'. Apparatus:

The complete carbonization apparatus is shown in Figure II. The electric resistance furnace (A) was the same as described in Figure I. Exact temperature regulation was secured by means of the resistance (B). The coking retort (C) was made of pyrex glass tubing 50 mm. in diameter and 30 cm. long. A 10mm. tube or side arm (D) was sealed on about 10 cm. from the top of the retort. The retort was held in the furnace in a vertical position with the upper 10 to 15 centimeters exposed. Asbestos paper was wrapped around the exposed portion to aid in distilling over the tar. The top of the retort was closed with a #8 one hole rubber stopper carrying a pyrex thermocouple tube (E). The stopper was protected from heat by three aluminum discs (F) placed on the thermocouple tube. The retort acted as a distilling flask with the side arm long enough to act as a condenser. The end of the side arm extended well into a 50 cc. distilling flask (G) in which the water and tar were collected. The evolved gas passed out through the side arm of the small distilling flask into a small bulb (H) filled with glass wool, used to remove





the tar fog. The U tubes (I and J) held dilute sulphuric acid for the removal of ammonia from the gas. During runs on the residue from the selenium oxychloride extraction these tubes also removed traces of selenium from the gas. One of these U tubes was filled with lead acetate, when desired, to remove hydrogen sulphide and hydrogen selenide. From this purification train the gas passed directly into a 12 liter aspirator bottle (L) which served as a gas holder. This bottle was graduated into 25 cc. divisions and the gas volume was measured here as well.

### 3'. Temperature Control and Measurement:

The furnace and resistance block have been previously mentioned. Some runs were made without resistance thus allowing the coking process to proceed as rapidly as possible. Others were conducted more slowly. The time and temperatures used are given in the tables of data. In general the temperature was not carried past 625°C so as to guard against any secondary decomposition of the products. Temperature readings of the furnace and retort were taken approximately every fifteen minutes. For temperature readings two Chromel-Alumel thermocouples (K) made of number 16 wire were used. These were connected as shown in Figure II. to a Weston Direct Current Millivoltmeter (M). They were standardized against the freezing points of Bureau of Standards Aluminum and Tin. The couples were exact duplicates and the same temperature curve was used for both. The temperature could be read from the curve to within two degrees and the couples were accurate to the same extent.

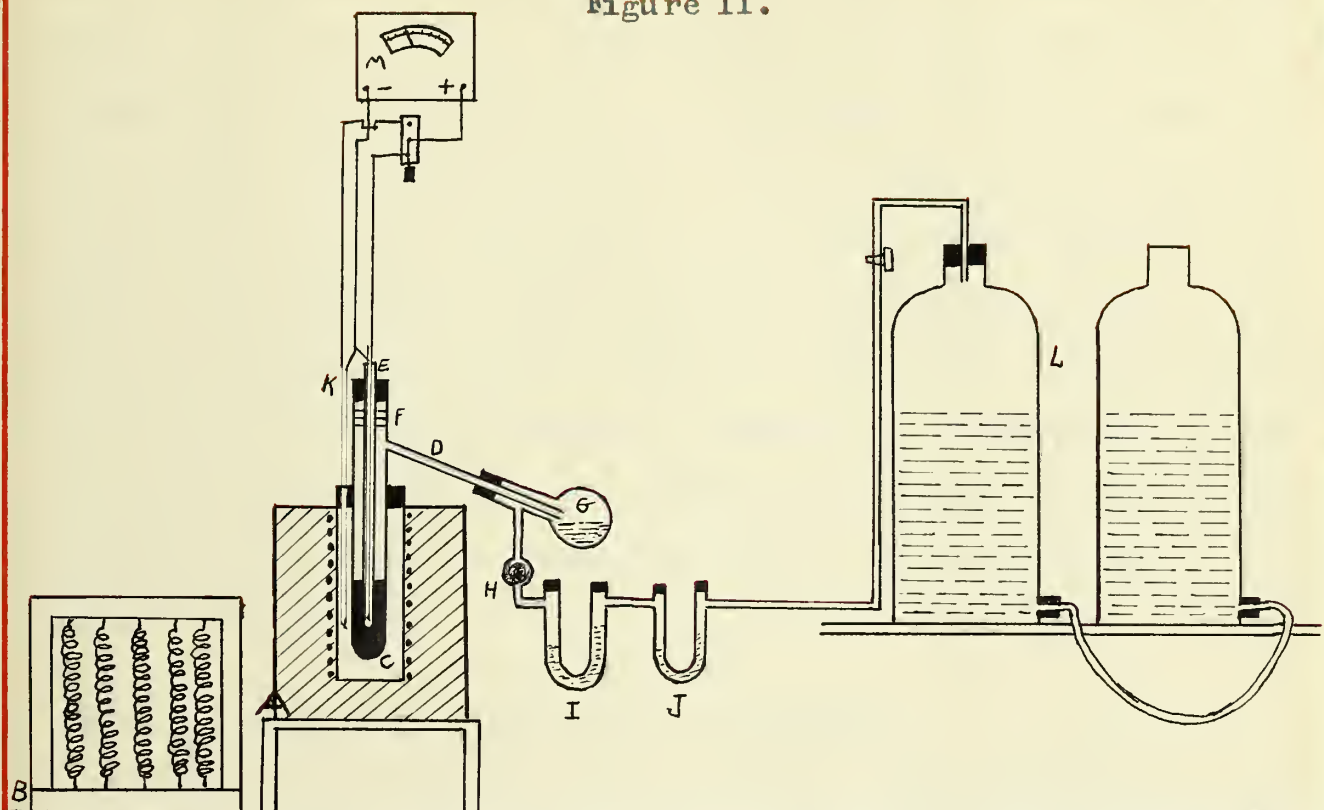
### 4'. Procedure:

Thirty grams of fresh coal, or residue under observation, air





Figure II.



- A - Electric Resistance Furnace
- B - Resistance Board
- C - Pyrex Glass Retort
- D - Side-arm Condenser
- E - Pyrex Glass Thermocouple Tube
- F - Aluminum Discs
- G - Tar Trap
- H - Glass Wool
- I - U Tube ( 10%  $\text{H}_2\text{SO}_4$  )
- J - U Tube ( Pb acetate )
- K - Thermocouples
- L - Aspirator Bottle 12l.
- M - Millivoltmeter



dried and ground to 60 mesh were poured into the retort. The thermocouple tube and stopper were inserted so that the lower end of the thermocouple tube extended down three-fourths of the way into the coal charge. All connections were made as shown, and the apparatus exhausted of air. The aspirator bottles were used to exhaust the air. During the carbonization run a suction was maintained upon the retort by holding the leveling aspirator bottle full length below the gas holder. No further attempt to control the pressure in the retort was made. The suction was sufficient to take off all volatile products as rapidly as formed and thus no secondary heating of products resulted.

#### 5'. Determination of Products and Analysis:

As has been stated in the outline the most important products from these carbonization tests were the residues, the tar and the gas. The amount of residue was determined by weighing. After weighing the coke, or semi-coke as the case might be, was sealed in a small sample bottle. The water and tar collected together in the tar trap were removed and centrifuged. Very few attempts were made to determine the weight of the water. The water was separated from the tar by use of a small pipette and the tar weighed. No attempt was made to determine the ammonia. The gas evolved was collected and measured in the gas holder. Portions representative of the whole were removed from the holder and analyzed in a Modified Orsat Apparatus (29), designed and built in this laboratory. The constituents were determined as follows:  $\text{CO}_2$  by absorption in  $\text{KOH}$ ,  $\text{O}_2$  in alkaline pyrogallol,  $\text{C}_2\text{H}_4$  in bromine water, and  $\text{C}_6\text{H}_6$  in fuming sulfuric acid.  $\text{H}_2$  and  $\text{CO}$  were burned in a copper oxide furnace at  $300^\circ\text{C}$ ., the  $\text{H}_2$  determined by contraction and the  $\text{CO}$  by absorption of the resulting  $\text{CO}_2$





in KOH.  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  were burned in an atmosphere of oxygen over mercury in a glass bulb and the two gases calculated by Earnshaw's (30) method.  $\text{N}_2$  was taken as the difference between the total of the above mentioned constituents and the original volume which was always taken as exactly 100 cc. thus giving the values obtained in percentage by volume.

No attempt was made to analyze the tar. In tests during which hydrogen sulphide was not removed from the gas with lead acetate it was determined as  $\text{CO}_2$  in the gas analysis. The percentages of  $\text{H}_2\text{S}$  are so small however as not to materially effect the  $\text{CO}_2$ .

## VI. Results, Part II.

### 1. The Effect of the Tar and Volatile Content of Coal Upon the Resulting Action of Selenium oxychloride:

The loss of resinic extractable matter, that is tar and those hydrocarbons forming the volatile constituent of coal, results in lessening very greatly the action of selenium oxychloride upon coal. The reagent attacks coal in proportion to the amount of volatile matter present in the coal. Coke which has lost its volatile matter and tar is not effected. Partially coked coal retaining a portion of its tar is attacked giving a gummy extract difficult to filter, while with fresh coal the selenium oxychloride attacks the resinic material and unsaturated hydrocarbons. Tar is not thought of as existing in coal as tar. The reagent removes those hydrocarbons, more especially the unsaturated hydrocarbons, and those resins which when coked or distilled yield the tar. The resinous extract taken out by the reagent is not a pure resinic material, but a new compound formed by chemical action of the reagent upon the resinic material. This results in the gummy substance, which being mixed with selenium from



the decomposed reagent, makes filtering impossible. Water will not effect this extract, but alcohol will aid in the filtering of it.

The loss of the coking property of the coal at the same time as the loss of the tar material leads to the conclusion that the bonding material of the coal gives the tar or else, if the two are separate and distinct, they both are attacked by the reagent. A solvent to destroy the coking properties of a coal does not necessarily remove the tar also. Many common solvents being used in research at the present time will destroy the coking property of coal, but when the coal residue is coked it continues to yield tar, though probably not in such large quantities. Selenium oxychloride is unique in this respect that it is able to remove, in the small amounts of coal used, all traces of tar from the coal when distilled.

If the extracted resins or tar material was not changed chemically by the reagent it should be possible to separate it by hydrolysis of the reagent. Since adding water does not effect a separation but only the decomposition of some remaining selenium oxychloride, it is safe to assume that chemical action forming some additive compound has taken place. The residue should be cellulose-like material if the data we have is correct which assumes that selenium oxychloride will not attack cellulose. Just what the nature of the residue is will have to be determined by analysis and by the study of the gases formed by carbonization runs on the residue.

## 2. The Effect of Selenium oxychloride Upon Coal:

Selenium oxychloride extracts all the resinic constituent of coal leaving nothing which may be further extracted with the ordinary organic solvents. The action is not a solvent one but chemical in nature. Powdered coal is attacked with the evolution of heat.





The resinic and tar forming constituent of the coal is extracted leaving the cellulosic and mineral part of the coal. The reagent reacts at once with the extracted portion to form new complex compounds. A portion of the reagent is decomposed by the chemical action resulting in the deposition of red, amorphous selenium throughout the extracted material.

No quantitative extraction is possible, especially from the standpoint of the extract. There is an extract and a residual material, but the extract can not be isolated pure and separation of the reagent from the residue entails losses which prevent quantitative work. Benzene or some similar inactive substance must be used to protect the reagent from the air and to aid in filtering. The residue obtained by filtering may be made fairly pure by extraction with carbon disulphide and washing with ether. A small amount of selenium and chlorine are left in the residue due to decomposition of the reagent while in contact with the residue. A comparison of the original coal and the residue upon the Dry basis is shown in Table VII.

Table VII.

Analysis for:	Coal.	Residue.	Difference.
Volatile matter	35.42	65.31	+ 29.89
Ash	9.33	7.94	- 1.39
Fixed Carbon	55.25	26.75	- 28.50
Total Carbon	74.62	56.09	- 18.53
Sulfur	1.05	0.84	- 0.21
Nitrogen	1.55	1.54	- 0.01
Oxygen	8.55	28.34	+ 19.79
Hydrogen	4.90	5.25	+ 0.35
B. T. U.	13,280	9,261	- 4,019





Selenium oxychloride does not attack the nitrogen of the coal. Practically no difference was found in the nitrogen content of the coal and of the residue. This fact is varified by work on nitrogen of coal by V.Bosman (31) at this laboratory.

Ash shows a slight loss. This is not considered important since experimental error and a very little extraction of some ash constituent such as pyrites will account for this loss.

Sulfur shows a very slight loss. From this it may be concluded that the residue contains practically all of the sulfur. This is to be expected since the ash is practically unchanged. A trace of organic sulfur may have been extracted or extraction of a little pyrites, which is soluble in the reagent, would account for the slight loss in both the ash and sulfur.

The loss in carbon content is the largest. Probably a little over  $1/2$  the carbon of the coal is present in the residue. The carbon of the extract, that is the resinic constituent of coal, is composed of carbon in the form of unsaturated hydrocarbons and bitumen.

The volatile matter shows a large gain due to loss in ash and fixed carbon. The organic compounds, which when heated yield volatile carbon, are not attacked. The paraffins are included among these. There is a small error in the volatile matter due to the burning off of traces of selenium and chemicals such as benzene which make the volatile percent too high.

The heat value was lowered by 4,019 Btu. or 31% of the total heat value of the coal.

Any error in the analysis will show in the hydrogen and oxygen. The hydrogen shows a slight increase in the residue which may be due to experimental error. The oxygen content of the residue is of special interest. A gain of nearly 18% is shown which is the only



substantial gain in any single constituent of the coal. This leads to the conclusion that the coal bodies extracted were very low in oxygen and that there was a large amount of oxidation during the extraction process. This oxidation may have been mechanical oxidation or more probably may be the result of chemical action of the reagent. Oxidation was to be expected with such a reagent as selenium oxychloride.

### 3. The Primary Volatile Products of Coal:

Four direct carbonization runs were made first on the fresh coal. These runs were numbered 1, 2, 3 and 5. Data collected on these runs and analysis of the gas is shown in Tables VIII, IX, X, and XI. In these four coking runs no resistance was used and the temperature was allowed to rise until the point set for the conclusion of the run was reached. In general the run was terminated when the tar had all been distilled over.

Three fractional carbonization runs were then made, runs number 6, 7, and 8. In these runs resistance was used and the coal charge heated up slowly in order to get the maximum yield of products up to any certain temperature. In Run 6 and 7 two cuts were made in the collection of gas. The first fraction or cut contained the gas evolved up to the point at which the tar begins to distil. The second fraction consisted of the gas given off while the tar was distilling, and the last fraction was that collected after all the tar had been removed from the coal. In Run 8 one more fractional cut was made to differentiate more fully between the gases evolved after the tar had been distilled and as the temperature reached the point of secondary decomposition. Data on these runs and the corresponding gas analysis is shown in Tables XII, XIII, and XIV.





## DATA ON DIRECT CARBONIZATION RUN #1.

Weight Coal 30 gm. Air dried Makitan, Franklin CO.  
 Residue 21.74 " = 72.46 %  
 Tar 1.52 " = 5.00

Type of residue: Good coke around thermocouple tube and out for about half the diameter of the coke.

## Combined Data on run:

Time	Temp. Outside	Temp. Center	Gas Volume	Remarks
0 '00"	Room	Room	0	
20	190	90	190	Moisture
40	340	250	390	
50	375	305	425	Much water over
1 00	410	400	550	First tar
1 10	430	400	750	
1 20	455	445	1050	
1 30	470	460	1350	
1 40	490	480	1660	
1 50	505	505	2075	
2 00	510	510	2300	Tar still coming
2 10	520	530	2500	
2 20	520	540	2750	
2 30	525	545	2980	
2 40	535	555	3200	
2 50	-	565	3370	
3 00	560	565	3450	
3 10	565	580	3700	
4 10	575	610	4400	
4 20	575	615	4500	

Remarks: A large retort was used and quite a little tar stuck to inner wall of retort, thus giving low yield in trap.

Gas Data:	Duplicate analyses.		Average
	I	II	
Temperature maximum	615°		
Time in hours	4.33		
Total gas	4500 cc.		

Gas analysis-	%	cc.	%	cc.	%	cc.
CO <sub>2</sub>	3.5	158	6.0	270	4.8	216
O <sub>2</sub>	2.0	90	3.5	158	2.7	122
C <sub>2</sub> H <sub>4</sub>	2.6	117	2.4	108	2.5	118
C <sub>6</sub> H <sub>6</sub>	.1	5	.4	18	.3	13
H <sub>2</sub>	30.0	1350	22.2	999	26.1	1175
CO	4.5	203	6.4	288	5.5	247
CH <sub>4</sub>	28.1	1265	30.6	1375	29.3	1320
C <sub>2</sub> H <sub>6</sub>	7.6	343	7.6	343	7.6	343
N <sub>2</sub>	21.6	972	21.9	985	21.2	951



Table IX.  
DATA ON DIRECT CARBONIZATION RUN #2.

Weight Coal 30.00 gm. Air dry Makitan.  
Residue 20.8 " = 69.3%.  
Tar 3.8 " = 12.6

Type of residue: Same type of semi coke.

Combined data on run:

Time	Temp. Outside	Temp. Center	Gas Volume	Remarks
0 '00"	148	90	0	Note retort hot
15	265	155	200	
30	330	275	260	
1 00	340	450	1200	
1 15	430	455	1725	Tar still dist.
1 30	465	525	2500	
1 45	525	560	3000	
2 00	-	575	3450	" " "
2 15	-	590	3700	
2 30	575	620	4000	
2 40	-	625	4200	
3 30	-	635	4800	" " "
4 30	630	650	5175	Tar all off
6 50	650	660	5700	

Gas Data:	Duplicate analyses		Average
	I	II	
Temperature maximum	660'		
Time in hours	6.8		
Total gas	5700 cc.		

Gas analysis-	%	cc.	%	cc.	%	cc. N <sub>2</sub> free
CO <sub>2</sub>	3.0	171	2.5	142	2.7	154 3.1
O <sub>2</sub>	2.0	114	2.1	120	2.1	120 2.4
C <sub>2</sub> H <sub>4</sub>	2.0	114	1.8	103	1.9	108 2.2
C <sub>6</sub> H <sub>6</sub>	.5	29	.6	34	.6	34 .7
H <sub>2</sub>	34.5	1967	33.2	1890	33.8	1928 39.4
CO	7.7	438	7.1	404	7.4	422 8.6
CH <sub>4</sub>	29.7	1690	35.3	2015	32.5	1852 37.8
C <sub>2</sub> H <sub>6</sub>	7.0	399	3.2	182	5.1	291 5.8
N <sub>2</sub>	13.6	775	14.2	808	13.9	793 0.0



Table X.

## DATA ON DIRECT CARBONIZATION RUN # 3.

Weight Coal 30.00 gm. Air dried Makitan  
 Residue 22.07 " = 73.5%  
 Tar 3.6 " = 12.0

Type of residue: About half coked.

Combined data on run:

Time	Temp. Outside	Temp. Center	Gas Volume	Remarks.
0 '00"	Room	Room	0	
40	300	200	250	
1 10	415	360	400	Much water off
1 45	425	375	450	Tar starting
1 55	450	415	680	
2 00	485	455	1100	
2 15	500	480	1500	
2 30	525	500	1900	Tar still coming
2 45	560	540	2500	White fumes
3 05	590	565	3050	

Gas data:

Duplicate analyses

I

II

Average

Temperature maximum 565°

Time in hours 3.00

Total gas 3050 cc.

Gas analysis:	N <sub>2</sub> free	%	cc.	%	cc.	%	CC.
CO <sub>2</sub>	4.3	3.0	92	3.5	107	3.3	101
O <sub>2</sub>	5.6	4.4	134	4.3	131	4.3	131
C <sub>2</sub> H <sub>4</sub>	3.9	3.0	92	3.0	92	3.0	92
C <sub>3</sub> H <sub>6</sub>	.8	.7	21	.6	18	.6	18
H <sub>2</sub>	27.4	20.4	622	21.6	660	21.0	641
CO	7.7	5.6	171	6.2	189	5.9	180
CH <sub>4</sub>	43.1	35.4	1082	30.6	935	33.0	1007
C <sub>2</sub> H <sub>6</sub>	7.2	4.4	134	6.7	204	5.5	168
N <sub>2</sub>	0.0	23.1	705	23.5	717	23.4	713





Table XI.

## DATA ON DIRECT CARBONIZATION RUN # 5.

Weight Coal 30.00 grm. Air dried Makitan.  
 Residue 22.98 " = 76.6%  
 Tar 1.69 " = 5.7

Type of residue: Excellent coke. Hard and whole mass coked.

## Combined data on run:

Time	Temp. Outside	Temp. Center	Gas Volume	Remarks
0 '00"	Room	Room	0	Occluded gas at 40'
15	110	55	90	
30	240	155	230	Moisture on retort
45	310	285	300	Water over
1 00	355	345	425	Tar at 400'
1 20	-	445	1000	
1 25	500	470	1250	
1 40	525	505	1800	
1 55	-	530	2450	Tar off

## Gas analysis data:

## Duplicate analyses

I II Average

Temperature maximum 530'  
 Time in hours 2.0  
 Total gas 2450 cc.

Gas analysis:	%	cc.	%	cc.	%	N <sub>2</sub> free
CO <sub>2</sub>	2.6		2.3		2.5	3.7
O <sub>2</sub>	6.4		6.6		6.5	9.7
C <sub>2</sub> H <sub>4</sub>	3.5		3.9		3.7	5.5
C <sub>6</sub> H <sub>6</sub>	.7		.7		.7	1.0
H <sub>2</sub>	12.3		11.5		11.9	17.8
CO	4.4		5.4		4.9	7.3
CH <sub>4</sub>	26.8		30.4		28.6	43.0
C <sub>2</sub> H <sub>6</sub>	9.4		6.7		8.0	12.0
N <sub>2</sub>	33.9		32.5		33.2	0.0

In Figure III. are plotted the curves for these coke runs. The time is plotted against temperature. The curves in black ink are for the four direct carbonization runs, and those in green for the three fractional runs. Figure IV. shows the time plotted against the volume of gas evolved, and Figure V. the temperature against the volume of gas. The same colors are used throughout to indicate certain coke runs.

Figures VI. to XIV. inclusive show graphs of the individual constituents of the gas as analyzed. Percentage composition is



plotted against the temperature. Each small circle on the graphs indicates the percentage composition of that constituent in the gas fraction for that temperature. The rise or fall of any certain constituent of the gas during any given temperature cut or fraction may be determined by reading the curve between the points representing the two cuts in question. A glance at the charts will show that of the four direct carbonization runs Number 2 curves vary considerable from Numbers 1, 3, and 5 which all lie practically together. Number 2 may therefore be omitted from consideration when drawing conclusions. One of the three fractional carbonization curves, #6, also shows a divergence in nearly all the charts from the other two which run practically together. Numbers 7 and 8 may therefore be taken as standard curves.

A study of the Tables and Figures submitted in connection with the seven direct and fractional coking runs made on fresh coal shows the following facts:

Coke- The residues varied from a semi-coke to well coked mass. Very different results were obtained from Taylor and Porter's (32) work in which they state that "slow carbonization tends to increase the yield of coke". Table XV. giving the percentage yields of coke and the time of the run for the direct carbonization runs 1, 2, 3 and 5 shows that the yield of coke for these runs was inversely proportional to the length of the run. The best coke came from the runs of shortest length.

Table XV.

Run	Yield of coke	Time in hours
2	69.3	6.8
1	72.46	4.3
3	73.5	3.0
5	76.6	2.0

The average yield of coke for the seven runs was 72.1%.





Tar- The average yield of tar for the seven runs was 8.2%. In general the higher the temperature and the longer the period of carbonization the larger was the yield of tar. The first sign of tar coming over varied from 335'-400'C., with an average of 385'C. This average temperature of the first appearance of tar is just ten degrees higher than the softening point of the coal 375'C. The tar was all off from 505'-650'C. The average temperature of the end point of tar distillation being 558'C.

Water- Water condensed out into the side arm of the retort at from 100'-230'C. Heavier condensation of water varied from 285' -365' with an average of 331'C.

Time and Temperature- During the four direct carbonization runs the temperature rose rapidly for one and one-fourth hours. At this time the temperature averaged around 390'C. From this point on the temperature rose much more gradually with the length of time. The point of falling off of temperature rise with time coincides with the start of the tar distillation.

Temperature and Volume of Gas- Figure V. shows that with the exception of Run 6, the volume of gas over at any certain temperature was approximately the same for all the runs. The fractional carbonization curves show a larger amount of gas at any temperature than the other four curves, naturally because the time was longer and resistance being in the coal was exposed to any given temperature for a longer time allowing more decomposition. However the difference is not great. The curves show that up to about 375' the evolution of gas is gradual. At this point there is a rapid evolution of gas which continues to about 450' after which the curves show a steady evolution of gas with no sudden changes. The distillation of



water of decomposition and tar is coincident with the rapid change in the rate of gas given off. Table XVI. shows the relation of temperature and time to the volume of gas.

Table XVI.

Run	Time in hours	Maximum Temp.	Volume of gas.
5	2.0	530	2450 cc.
3	3.0	565	3050
1	4.3	615	4500
2	6.8	660	5700

Carbon Dioxide- Analysis of gas fractions shows that  $\text{CO}_2$  is present below  $350^\circ\text{C}$ . It increases after the tar starts distilling and up to about  $525^\circ$  where the high point is reached. From this point on and in that portion of gas collected after the tar is all off the percentage of carbon dioxide rapidly decreases. Less than 2% remains in gas at  $625^\circ\text{C}$ . The data tables for runs 1, 2, 3 and 5 show that the total amount of carbon dioxide yielded increased in the order of runs 5-3-1 and then fell off rapidly in run 2. Table XVI. shows that 5-3-1 is the order of runs in which time, temperature and gas volume increased. Run 2 which took the longest time and reached the highest maximum temperature shows the smallest amount of total  $\text{CO}_2$ . We may conclude that  $\text{CO}_2$  increases with temperature up to about  $615^\circ$  as shown in the graph, and then rapidly falls off as the temperature increases and secondary decomposition begins.

Oxygen- Analysis of fractional cuts of gas shows high oxygen content below  $350^\circ$ . As the tar distills the percentage of oxygen rapidly falls off. After the tar is off the oxygen remains practically the same until  $600^\circ$  is reached after which it falls. The totals show that oxygen content decreased in the order of runs 5-3-1-2 as





the temperature, time and gas volume increased. Oxygen is present in highest quantities in the first gas given off by carbonization of coal. Much of this is held mechanically and is due to weathering.

Unsaturated Hydrocarbons- are very low in gas given off by coal before the tar starts to distill. From 375' the percentage rapidly increases until a temperature of approximately 525' is reached. From then on until 625' the percentage falls, practically no unsaturated hydrocarbons coming off above 625'C.

Benzene or Saturated Aromatics- The curves for benzene are nearly identical with those for the unsaturated paraffins. There is quite a little variation in the benzene curves due to the fact that such small amounts are present. Benzene is formed from the unsaturated paraffins upon the distillation of the coal and therefore its content in gas depends upon the amount of ethylene present.

Carbon Monoxide- Only a small amount of CO is found in gas below 375'C. Incomplete oxidation of cellulose upon decomposition accounts for its presence at this stage. From the point of distillation of tar up until the CO<sub>2</sub> begins to decompose the percentage of CO slowly increases. From 600' on there is a rapid rise.

Ethane- is practically all given off during the time the tar is distilling. Rise and fall are very sudden.

Methane- goes parallel to ethane. Practically all is given off while the tar distils.

Hydrogen- A small amount of hydrogen is given off before the tar begins to distil due to decomposition of cellulose. From 375' the rise is very rapid. There are two points of sudden rise. First about 560' when the resinic material starts to decompose rapidly, and second after 650' when secondary decomposition is beginning.





Table XII.

## DATA ON FRACTIONAL CARBONIZATION RUN #6.

Weight Coal 30.00 gm. Fresh Makitan.  
 Residue 21.20 " = 70.9%  
 Tar 2.00 " = 6.7

Type of residue: Semi coke.

## Combined data on run:

Time	Temperature	Gas Volume	Remarks
0 '00"	Room	0	
3.00	365	1375	First tar
	First cut -		
0 00	365	0	
6 45	525	4550	Much water and tar
	Second cut -		
0 00	525	0	
2 25	620	1900	
	Last cut -		

## Gas Data:

## Fractions or Cuts

	I	II	III	Total
Temperature	365	525	620	620
Time in hours	3.0	6.75	2.42	12.2
Total Gas	1375 cc	4550 cc	1900 cc	7825 cc
Gas analysis:	% cc.	% cc.	% cc.	% cc.
CO <sub>2</sub>	0.0 0	6.7 305	1.0 19	4.1 324
O <sub>2</sub>	18.3 251	4.8 218	5.8 110	7.4 579
C <sub>2</sub> H <sub>4</sub>	.2 3	1.7 78	.2 4	1.1 85
C <sub>6</sub> H <sub>6</sub>	0.0 0	.5 23	.2 4	.3 27
H <sub>2</sub>	1.0 14	22.8 1038	55.0 1045	26.8 2097
CO	1.9 26	6.9 314	7.0 133	6.0 473
CH <sub>4</sub>	0.1 1	27.3 1242	26.8 518	22.5 1761
C <sub>2</sub> H <sub>6</sub>	0.0 0	3.7 168	1.3 25	2.5 193
N <sub>2</sub>	78.5 1080	25.6 1164	2.7 42	29.3 2286

## Nitrogen free-

CO <sub>2</sub>	0.0	9.0	1.0	5.8
O <sub>2</sub>	85.1	6.5	6.0	10.5
C <sub>2</sub> H <sub>4</sub>	.9	2.3	.2	1.6
C <sub>6</sub> H <sub>6</sub>	0.0	.7	.2	.4
H <sub>2</sub>	4.7	30.6	56.5	38.0
CO	8.8	9.3	7.2	8.5
CH <sub>4</sub>	.5	36.8	27.6	31.7
C <sub>2</sub> H <sub>6</sub>	0.0	4.8	1.3	3.5



Table XIII.

## DATA ON FRACTIONAL CARBONIZATION RUN # 7.

Weight Coal 30.00 gm. Fresh Makitan  
 Residue 21.05 " = 70.1%  
 Tar 2.20 " = 7.3

Type of residue: Semi coke. Not hard but extremely fragile.

Combined data on run:

Time	Temperature	Gas Volume	Remarks
0 '00"	Room	0	
2 30	395	600	First tar over
	First cut -		
0 00	395	0	
4 30	565	3000	
	Second cut -		
0 00	570	0	
1 50	620	1500	
	Last cut -		

Gas data:

Fractions or Cuts

	I	II	III	Total
Temperature	395'	565'	620'	620'
Time in hours	2.5	4.5	1.8	8.8
Total gas	600	3000	1500	5100

Gas analysis:	%	cc.	%	cc.	%	cc.	%	cc.
CO <sub>2</sub>	4.9	29	5.1	153	1.8	27	4.1	209
O <sub>2</sub>	15.2	91	.9	27	2.8	42	3.2	160
C <sub>2</sub> H <sub>4</sub>	.6	4	2.9	87	.3	4	1.9	95
C <sub>6</sub> H <sub>6</sub>	0.0	0	.7	21	.1	1	.5	22
H <sub>2</sub>	18.0	108	20.0	600	54.0	810	29.8	1518
CO	2.3	14	8.4	252	8.5	128	7.7	394
CH <sub>4</sub>	13.5	81	27.8	834	27.0	405	25.8	1320
C <sub>2</sub> H <sub>6</sub>	1.0	6	9.0	270	1.2	18	5.7	294
N <sub>2</sub>	44.5	267	25.2	756	4.3	65	21.3	1088

Nitrogen free -

	%	cc.	%	cc.
CO <sub>2</sub>	8.8	6.8	1.9	5.2
O <sub>2</sub>	27.5	1.2	2.9	4.0
C <sub>2</sub> H <sub>4</sub>	1.1	3.9	.3	2.4
C <sub>6</sub> H <sub>6</sub>	0.0	.9	.1	.6
H <sub>2</sub>	32.4	27.0	56.4	37.8
CO	4.2	11.4	8.9	9.8
CH <sub>4</sub>	24.3	37.2	28.2	32.8
C <sub>2</sub> H <sub>6</sub>	1.8	11.6	1.3	7.4
N <sub>2</sub>	0.0	0.0	0.0	0.0





Table XIV.

## DATA ON FRACTIONAL CARBONIZATION RUN #8.

Weight Coal	30.00	grm.	Fresh Makitan.
Residue	21.72	"	= 72.4%
Tar	2.40	"	= 8.0
Water	3.30	"	= 11.0

Type of residue: Semi coke. Not hard. Poor quality due to length of time of carbonization.

Gas Data:	Fractions or Cuts				
	I	II	III	IV	Total
Temperature	375'	505'	575'	620'	620'
Time in hours	4.2	3.25	3.00	0.5	11.0
Total gas	800	2500	1370	1100	5770
Gas analysis:	%	%	%	%	%
CO <sub>2</sub>	3.3	7.3	3.6	0.0	4.5
O <sub>2</sub>	16.4	2.5	2.2	1.0	4.1
C <sub>2</sub> H <sub>4</sub>	0.0	4.1	0.5	0.4	2.0
C <sub>6</sub> H <sub>6</sub>	0.0	1.0	0.0	0.0	.4
H <sub>2</sub>	0.8	19.1	27.2	54.6	25.2
CO	1.3	3.5	10.4	8.3	5.7
CH <sub>4</sub>	0.3	21.2	32.2	29.5	22.6
C <sub>2</sub> H <sub>6</sub>	0.0	8.6	0.0	1.4	4.0
N <sub>2</sub>	77.9	32.7	23.9	4.8	31.5

## Combined data on run:

Time	Temperature	Gas Volume	Remarks
0 '00"	Room	0	
	100		Sign of moisture
	240		Larger distillation of
1 40	265	400	water of decomposition.
1 50	285	400	
2 20	305	500	
2 45	330	540	
2 55	340	580	Much more water
4 10	375	800	First tar
	First cut -		
0 00	375	0	
20	385	200	
40	395	250	
1 00	420	500	
1 20	435	900	Tar still coming
1 40	455	1300	
3 05	495	2450	
3 15	505	2500	Last of tar
	Second cut -		
0 00	510	0	
2 30	520	1000	
3 05	575	1370	
	Third cut -		
0 00	580	0	
30	620	1100	





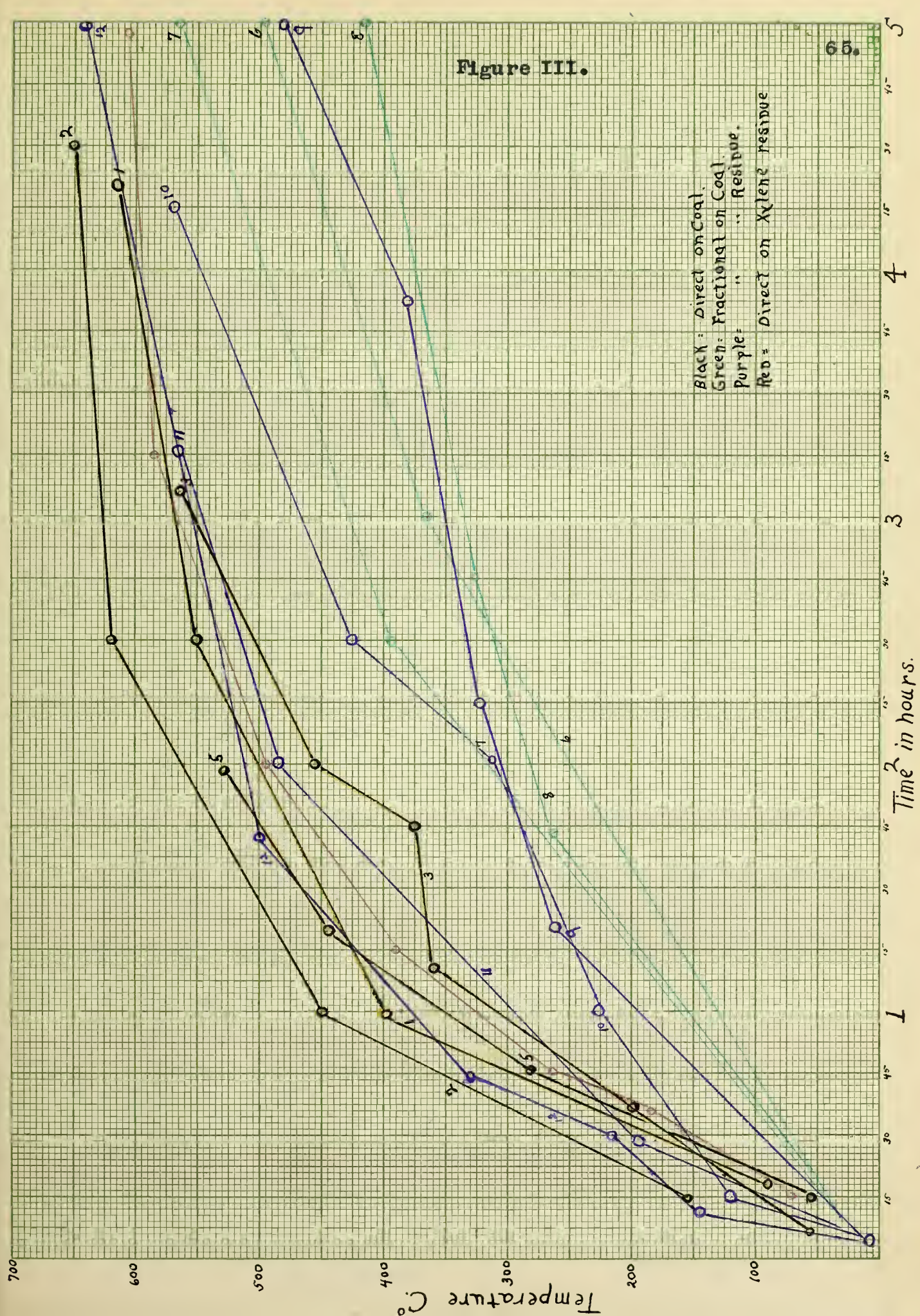






Figure IV.

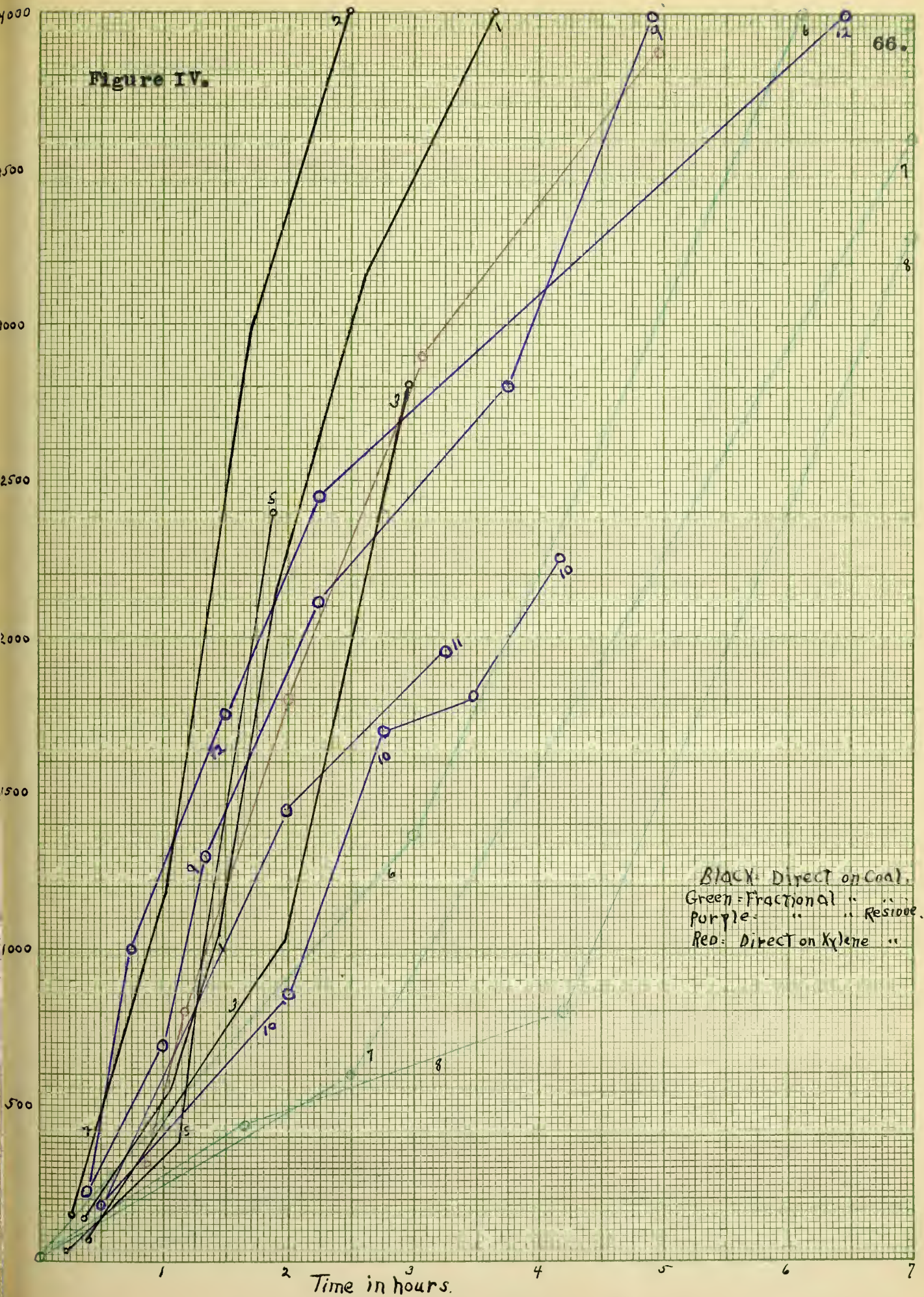
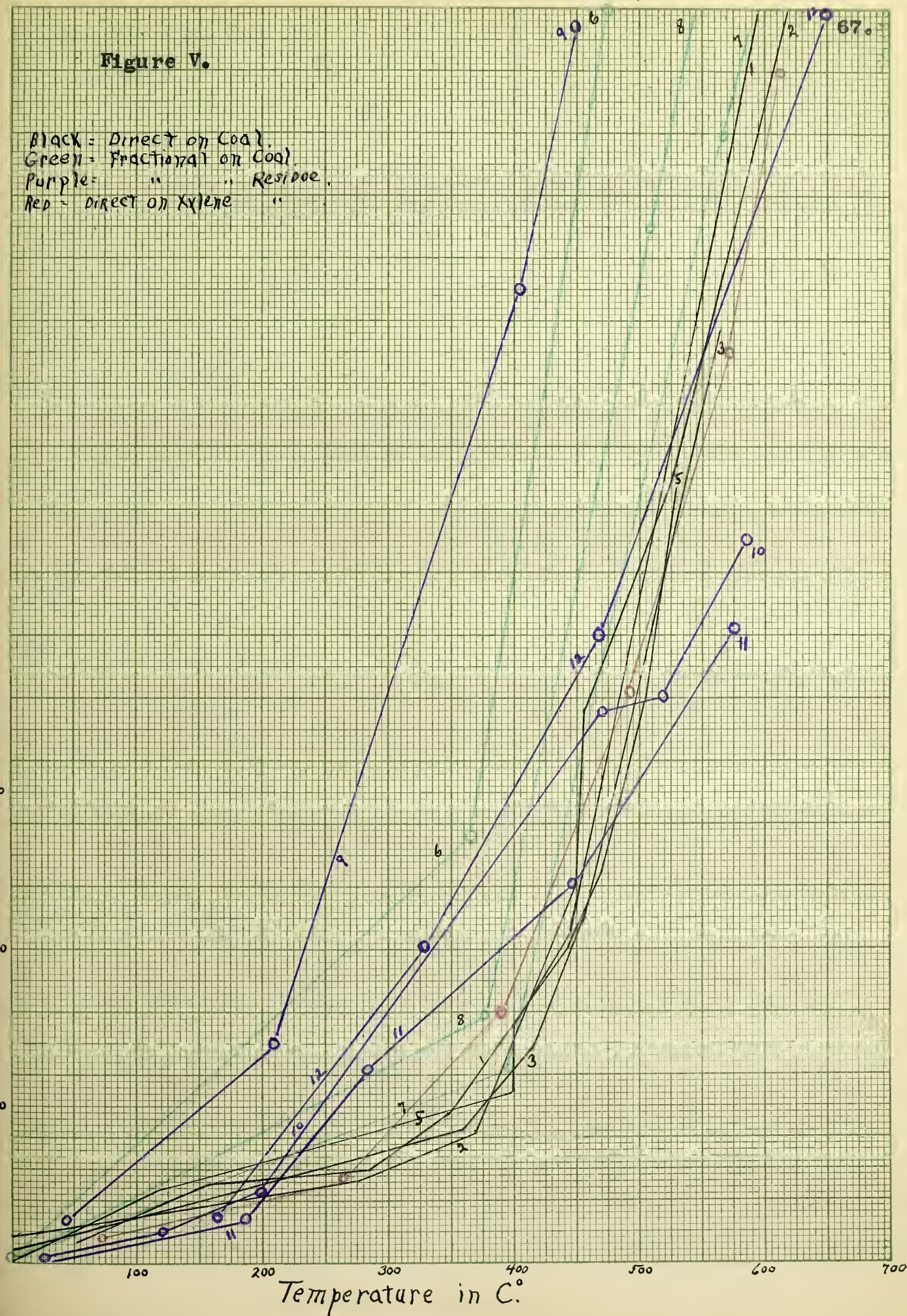






Figure V.

Black = Direct on Coal.  
 Green = Fractional on Coal.  
 Purple = " " Residue.  
 Red = Direct on Xylene "



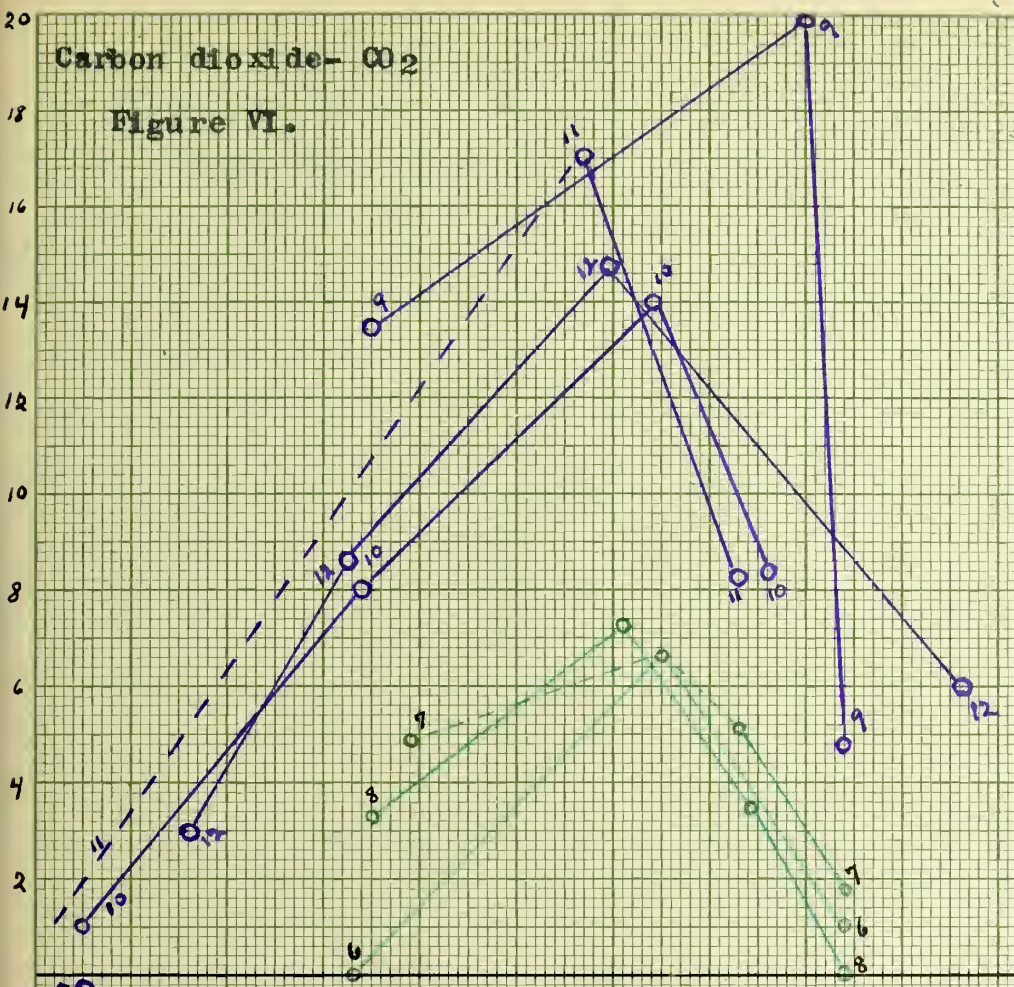




Carbon dioxide- CO<sub>2</sub>

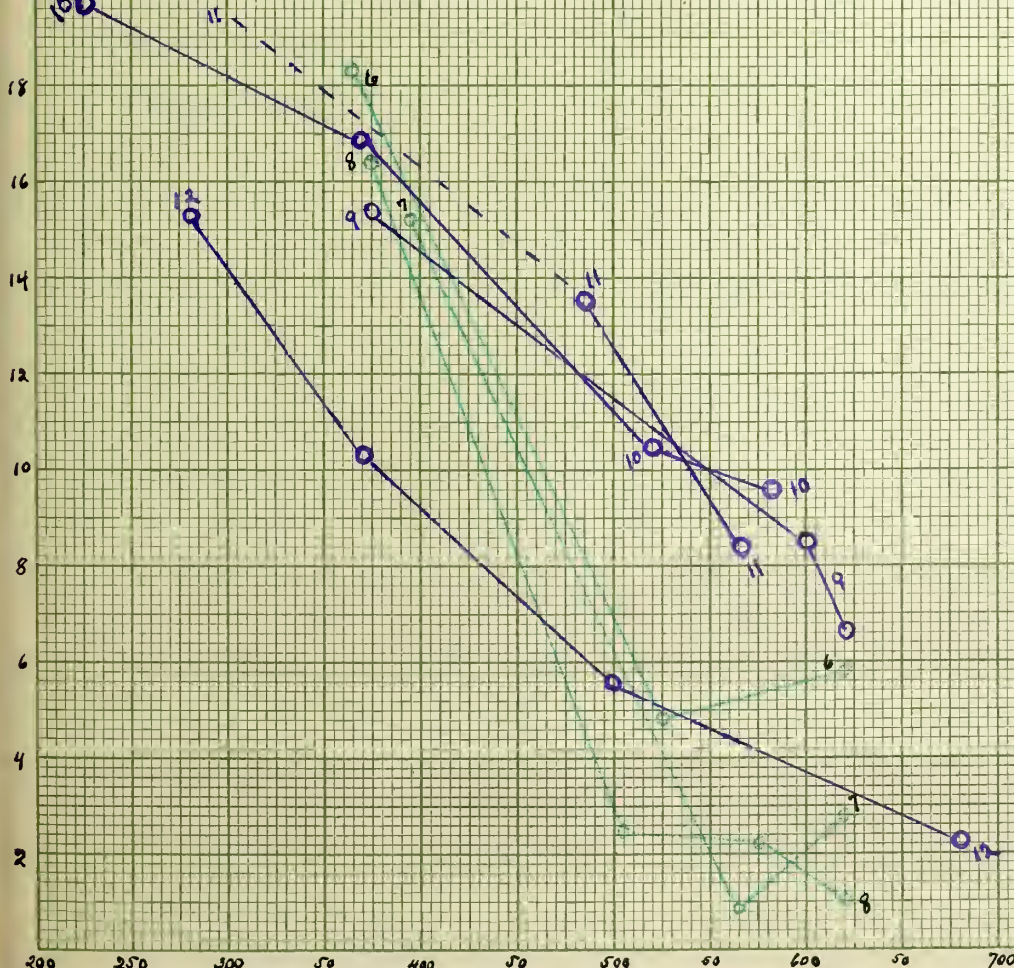
Figure VI.

Green = Coal.  
Purple = Residue.



Oxygen- O<sub>2</sub>

Figure VII.



Degrees Centigrade.







Ethylene-  $C_2H_4$ 

Figure VIII.

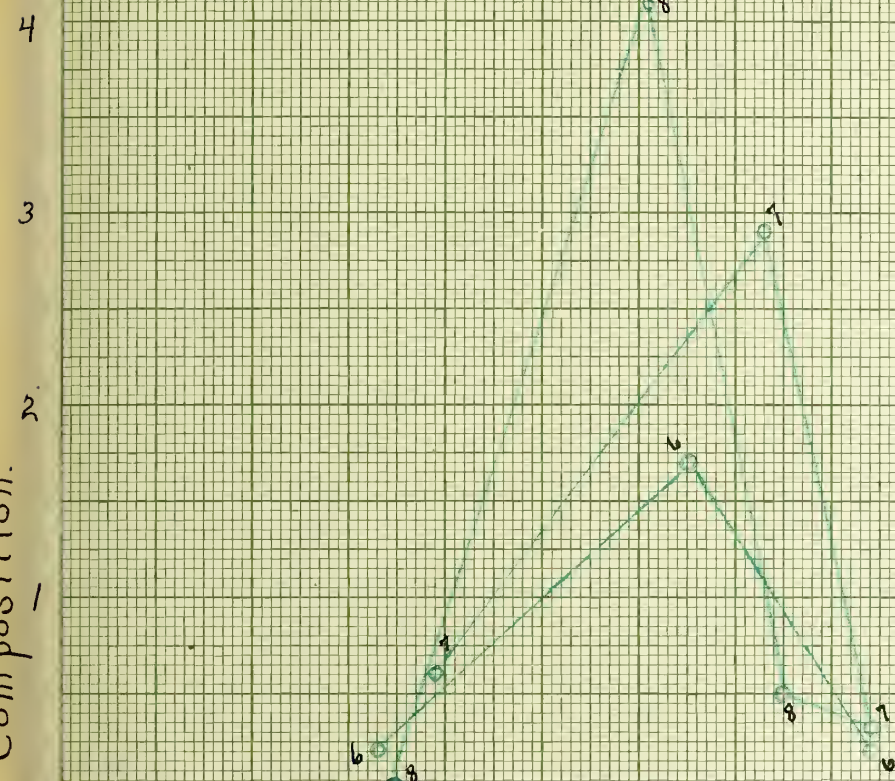
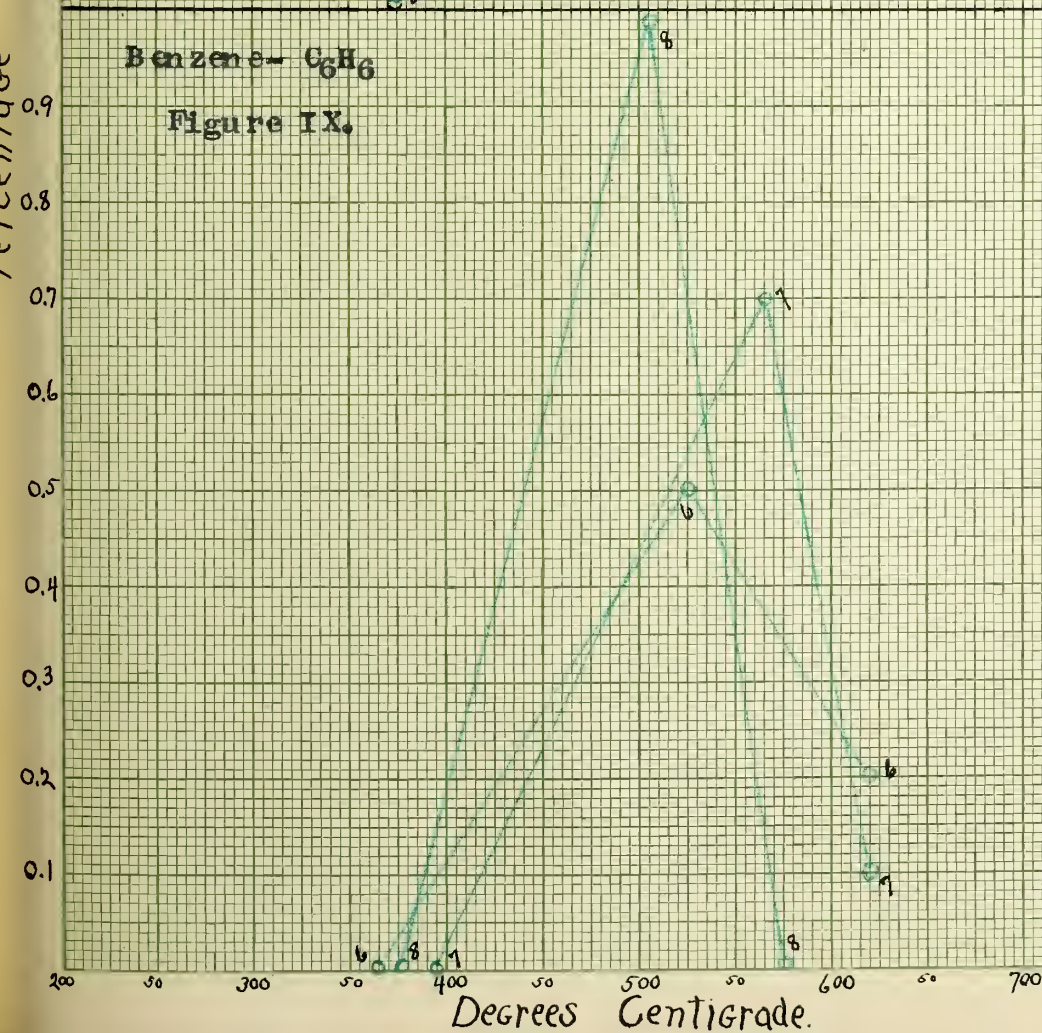
Benzene-  $C_6H_6$ 

Figure IX.

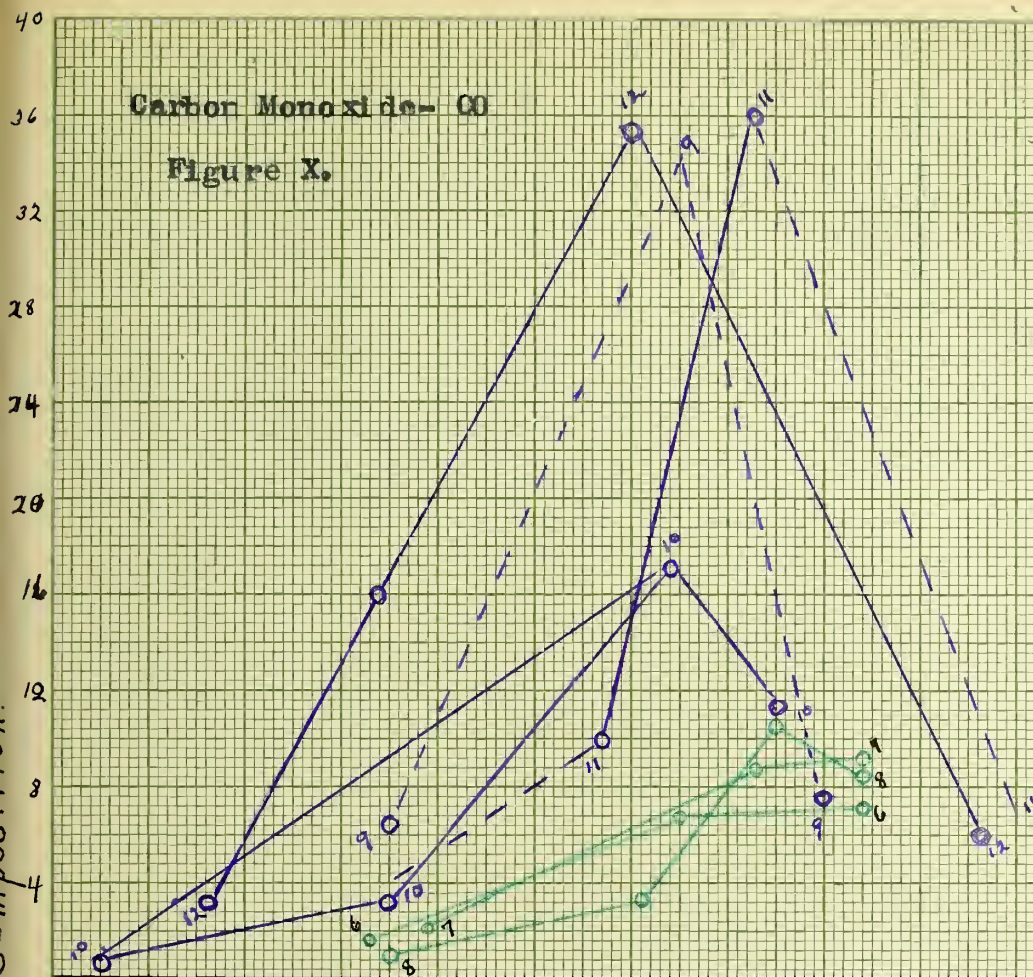






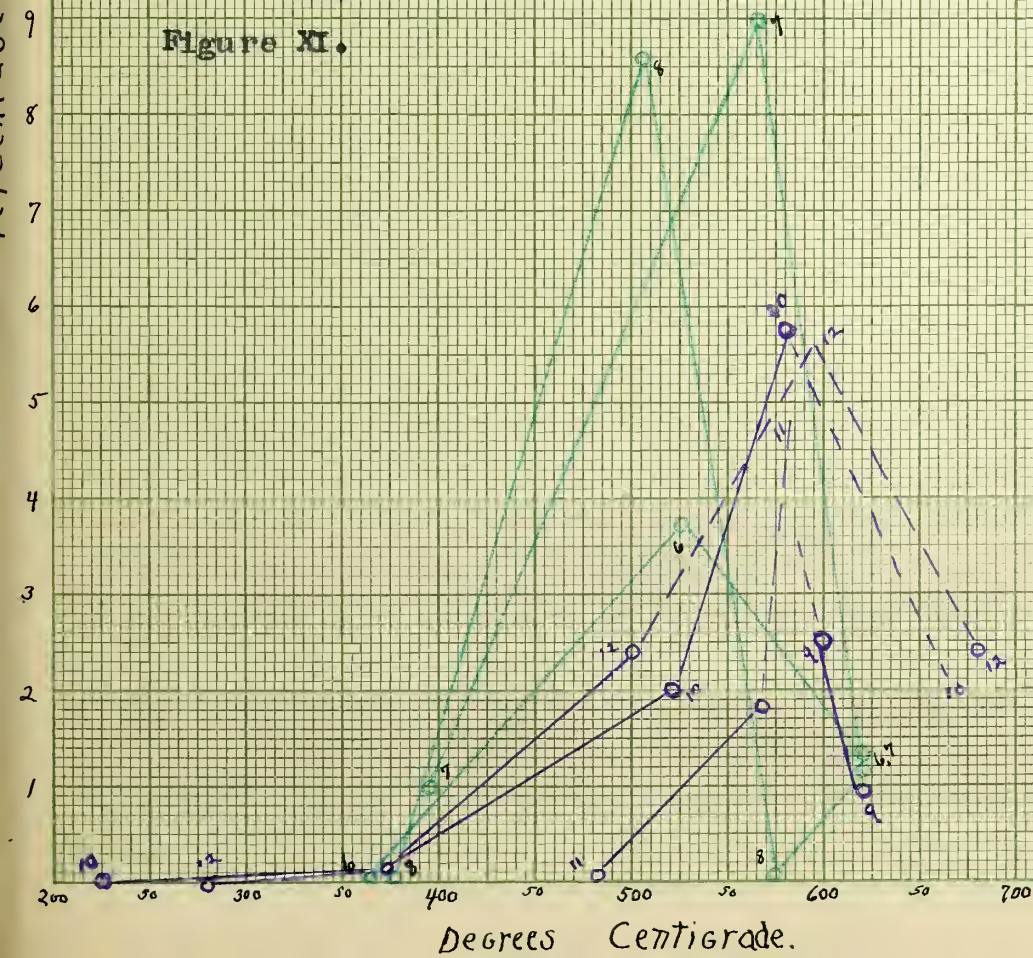
Carbon Monoxide- CO

Figure X.



Ethane- C<sub>2</sub>H<sub>6</sub>

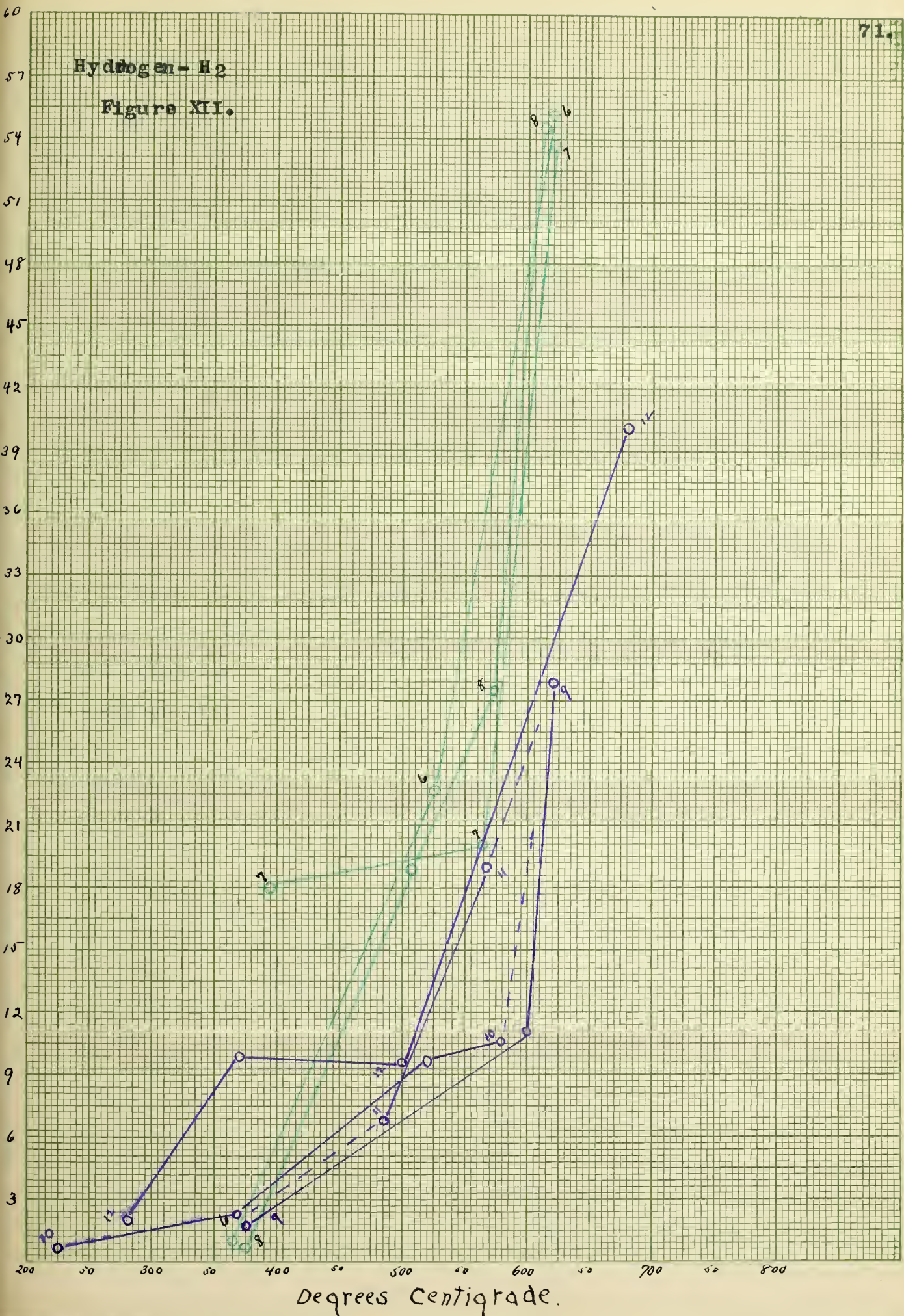
Figure XI.







Hydrogen - H<sub>2</sub>  
Figure XII.

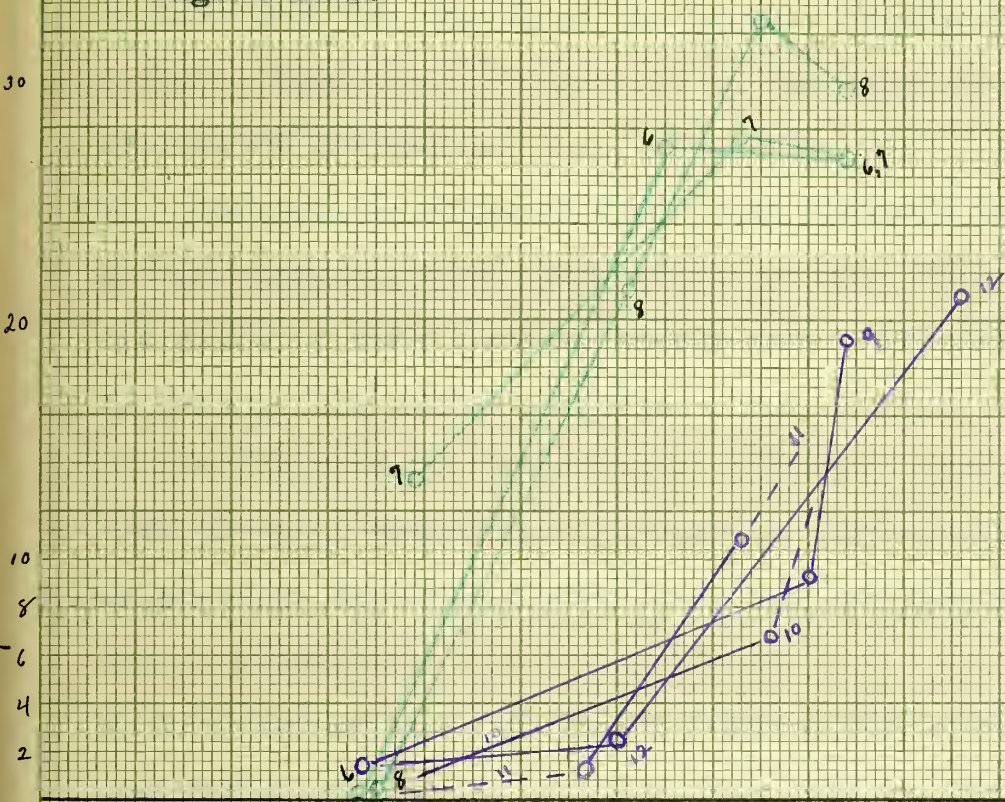






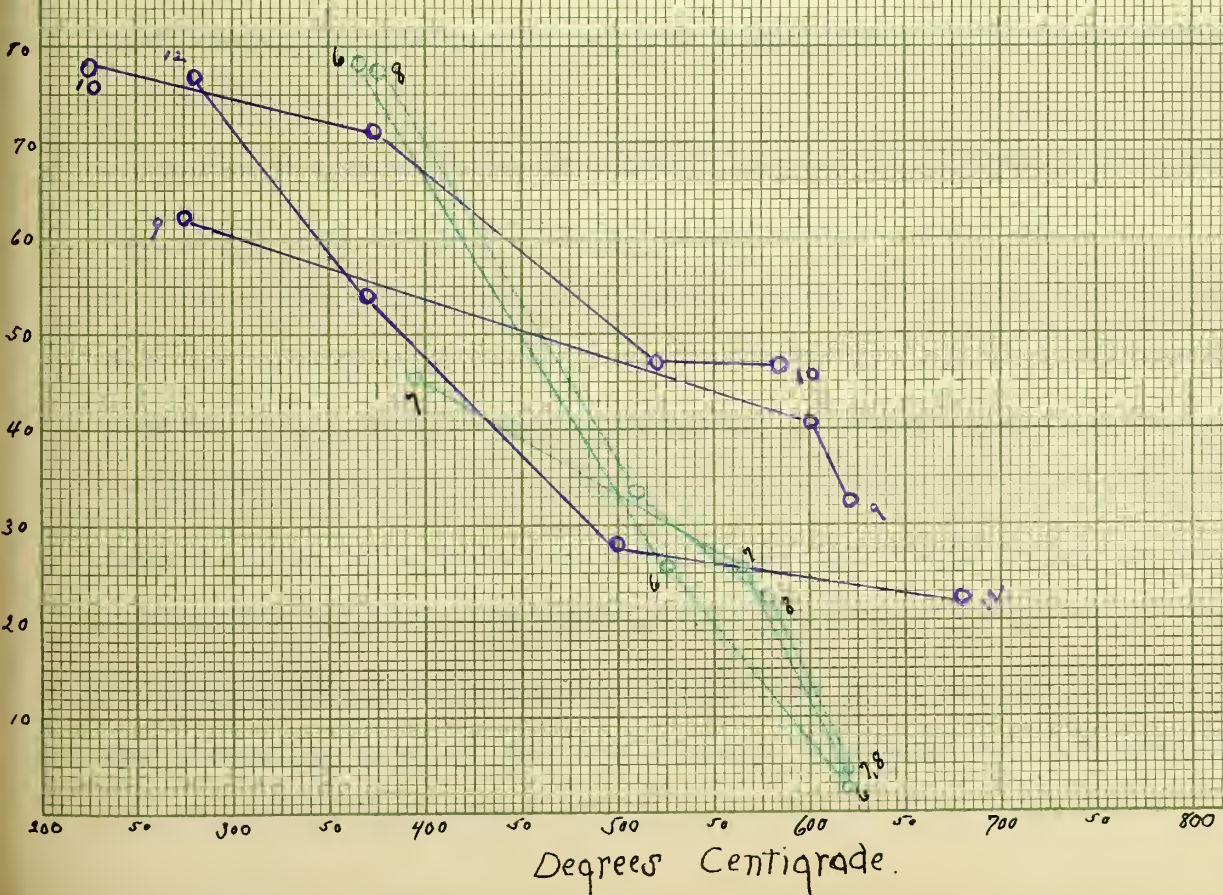
Methane-  $\text{CH}_4$

Figure XIII.



Nitrogen-  $\text{N}_2$

Figure XIV.







To summarize this data it may be stated that:

- 1- More than two-thirds of the organic substance of coal is decomposed at temperatures below 500°C. The remainder is mostly decomposed between 500°C-600°C.
- 2- Coke may be obtained from fresh Illinois coal of the type used in this investigation. Fast coking of the charge tends to increase the yield of coke. Heating slowly over a long length of time tends to destroy the coking property.
- 3- Low temperature carbonization yields a higher percentage of tar than the high temperature process. An average yield of 8.2% is obtained by the method here used. The tar begins to distil at 385°C and is practically all off by 560°C.
- 4- Ordinary moisture of coal is driven off at 105°C. Water of decomposition of coal is produced from coal in largest amounts above 250°C. This water of decomposition is mostly off by 500°C, the larger distillation coming around 330°C. The largest part of the water of coal then, consisting of moisture and water of decomposition, is out by 500°C.
- 5- Rise of temperature in coking retort proceeds more rapidly during the first two hours of carbonization than later on.
- 6- Coal breaks down at all temperatures more or less. At temperature of normal atmospheric temperature the process is one of oxidation or weathering. The temperature at which reactions occur to any extent in experimental time must be considered above atmospheric temperature. Bituminous coals of the type used begin to decompose and distil between 150°C-200°C.
- 7- The first decomposition occurring as the temperature is raised is the breaking down of the cellulosic substance of the coal. The first



primary products of decomposition being chiefly water of decomposition,  $\text{CO}$  and  $\text{CO}_2$ . At 285' the water of decomposition,  $\text{CO}$ ,  $\text{CO}_2$  and oxygen predominate.

8- At approximately 331' there is a large increase in the yield of gas accompanied by a larger amount of water of decomposition and small percentages of hydrogen. Organic compounds here begin to break down as evidenced by presence of  $\text{H}_2\text{S}$ . Liquid and gaseous hydrocarbons higher than methane have begun to distil before this.

9- At 385' comes a larger distillation of paraffin hydrocarbons. Tar unsaturated hydrocarbons, benzene, ethane and methane predominate.

10- At 450' there is a second heavy evolution of gas. Paraffin hydrocarbons,  $\text{CO}_2$ , and water of decomposition now predominate. The coal is still producing gases which kill the coking property by preventing the bonding together of the coal material.

11- Between 525'-600' the paraffins run out and  $\text{CO}_2$  begins to decompose increasing the yield of  $\text{CO}$  and oxygen. The yield of unsaturated hydrocarbons has reached a maximum and the hydrogen is increasing.

12- By 500' two thirds of the organic substance of the coal is decomposed. The last water of decomposition is coming over and the distillation of tar is falling off.

13- Between 625'-650' formation of benzene is stopped. The tar is practically all off and much more hydrogen is in evidence in the gas.

14- These tests were not carried to a higher temperature. Above 650' there is a final distillation of volatile matter from the heavier hydrocarbons and resinic material of the coal. Secondary decomposition sets in around 700'C.





Table XVII.

## DATA ON FRACTIONAL CARBONIZATION RUN #9 ON RESIDUE.

Weight charge 30.00 gm. Residue from selenium oxychloride ext.  
 residue 20.44 " = 68.1%

No tar and only a few cc. of water came off.

Dilute sulfuric acid and lead acetate bottles in train.

Type of residue: Fine powder in appearance like original charge.

## Combined data on run:

Time	Temperature	Gas Volume	Remarks
0 '00"	Room	0	
1 00	210	700	Much moisture vapor.
1 20	265	1300	
1 45	290	1700	
2 00	315	1900	
2 15	325	2100	
2 35	340	2300	
2 45	345	2400	
3 05	360	2550	Trace of Se shows
3 30	363	2750	
3 45	375	2800	
	First cut -		
0 00	375	0	
1 00	450	1050	
2 25	600	3100	
	Second cut -		
0 00	600	0	
10	605	300	
40	605	650	
55	620	900	
	Last cut -		

Gas Data:	Fractions or cuts			
	I	II	III	Total
Temperature	375'	600'	620'	620'
Time in hours	3.75	2.5	1.0	7.3
Total gas	2800	3100	900	6800

Gas analysis:	%	%	%	%	Nitrogen free basis -			
CO <sub>2</sub>	13.5	20.2	4.8	15.4	35.7	34.0	7.3	29.8
O <sub>2</sub>	15.5	8.5	6.7	11.1	40.9	14.3	9.9	21.4
C <sub>2</sub> H <sub>4</sub>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C <sub>6</sub> H <sub>6</sub>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H <sub>2</sub>	2.7	11.3	28.0	10.0	7.1	19.0	41.3	19.3
CO	6.1	7.7	7.8	7.2	16.3	12.9	11.5	13.9
CH <sub>4</sub>	Trace	9.3	19.4	6.8	0.0	15.6	28.6	13.1
C <sub>2</sub> H <sub>6</sub>	Trace	2.5	1.0	1.3	0.0	4.2	1.4	2.5
N <sub>2</sub>	62.2	40.5	32.3	48.2	0.0	0.0	0.0	0.0



Table XVIII.

## DATA ON FRACTIONAL CARBONIZATION RUN # 10 ON RESIDUE.

Weight of charge 15.00 gm.  
 residue 10.34 " = 69%

No tar.

Type of residue: Powder like original charge.

## Combined data on run:

Time	Temperature	Gas Volume	Remarks
0 '00"	Room	0	
15	120	100	
30	160	175	
45	195	220	
1 00	225	300	Much more water
First cut -			
0 00	225	0	
45	285	400	
1 15	370	900	
Second cut -			
0 00	370	0	
30	470	500	
1 00	485	550	
1 15	520	600	
Third cut -			
0 00	520	0	
30	570	350	
35	580	425	
Last cut -			

Gas Data:	Fractions or cuts				Total
	I	II	III	IV	
Temperature	225'	370'	520'	580'	580'
Time in hours	1.0	1.25	1.25	.55	4.0
Total gas	300	900	600	425	2225

Gas analysis:	%	%	%	%	%
CO <sub>2</sub>	1.0	8.0	14.0	8.4	8.8
O <sub>2</sub>	20.0	16.8	10.5	9.6	14.1
C <sub>2</sub> H <sub>4</sub>	0.0	0.0	0.0	0.0	0.0
C <sub>6</sub> H <sub>6</sub>	0.0	0.0	0.0	0.0	0.0
H <sub>2</sub>	0.5	1.7	9.5	10.0	5.2
CO	0.5	2.4	17.0	11.6	7.9
CH <sub>4</sub>	0.0	0.0	0.0	6.8	1.3
C <sub>2</sub> H <sub>6</sub>	0.0	0.0	2.0	5.8	1.6
N <sub>2</sub>	78.0	71.1	47.0	47.8	61.1





Table XIX.

## DATA ON FRACTIONAL CARBONIZATION RUN # 11 ON RESIDUE.

Weight charge 15.00 gm.  
 residue 10.42 " = 69.5%

No tar.

Type of residue: Powder.

## Combined data on run:

Time	Temperature	Gas Volume	Remarks
0 '00"	Room	0	
30	185	130	
1 00	280	600	
2 00	485	1450	
	First cut -		
0 00	485	0	
45	535	350	
1 15	565	500	
	Second cut -		

## Gas Data:

## Fractions

	I	II	Total
Temperature	485'	565'	565'
Time in hours	2.0	1.25	3.25
Total gas	1450	500	1950

## Gas analysis:

	%	%	%
CO <sub>2</sub>	17.0	8.3	14.9
O <sub>2</sub>	13.6	8.4	12.3
H <sub>2</sub>	6.5	19.4	9.9
CO	10.0	36.0	16.7
CH <sub>4</sub>	0.0	10.5	2.7
C <sub>2</sub> H <sub>6</sub>	0.0	1.8	0.4
N <sub>2</sub>	52.9	15.6	43.1

## Nitrogen free basis -

CO <sub>2</sub>	36.1	9.9	26.2
O <sub>2</sub>	28.8	9.9	21.6
H <sub>2</sub>	13.8	23.1	17.4
CO	21.3	42.6	29.4
CH <sub>4</sub>	0.0	12.4	4.7
C <sub>2</sub> H <sub>6</sub>	0.0	2.1	.7
N <sub>2</sub>	0.0	0.0	0.0



Table XX.

## DATA ON FRACTIONAL CARBONIZATION RUN # 12 ON RESIDUE.

Weight of charge 25.30 gm.  
 residue 16.25 " = 65%

No tar.

Type of residue: Powder.

Combined data on run<sup>4</sup>

Time	Temperature	Gas Volume
0 '00"	Room	0
40	280	700
First cut -		
0 00	280	0
15	370	600
Second cut -		
0 00	370	0
50	500	900
Third cut -		
0 00	500	0
15	510	250
7 20	680	2450

Gas Data:	Fractions				Total
	I	II	III	IV	
Temperature	280'	370'	500'	680'	680'
Time in hours	.75	.25	.90	8.33	9.2
Total gas	700	600	900	2450	4650

Gas analysis:	%	%	%	%	Nitrogen free			
CO <sub>2</sub>	3.0	8.2	15.0	6.0	12.6	18.4	21.4	7.7
O <sub>2</sub>	15.3	10.3	5.9	2.2	64.3	23.2	8.3	2.8
C <sub>2</sub> H <sub>4</sub>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C <sub>6</sub> H <sub>6</sub>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H <sub>2</sub>	2.0	10.0	9.3	40.0	8.4	22.4	13.3	51.4
CO	3.5	16.0	35.2	6.0	14.7	36.0	50.4	7.7
CH <sub>4</sub>	0.0	0.0	2.4	21.3	0.0	0.0	3.3	27.3
C <sub>2</sub> H <sub>6</sub>	0.0	0.0	2.4	2.4	0.0	0.0	3.3	3.1
N <sub>2</sub>	76.2	55.5	29.8	22.1	0.0	0.0	0.0	0.0

#### 4. The Effect of Selenium oxychloride Upon the Primary Volatile Products of Coal:

Four fractional carbonization runs were made upon the residue from the selenium oxychloride extraction of coal in exactly the same manner as upon the fresh coal. These runs were numbered 9, 10, 11, and 12. Data and gas analysis for these runs are given in Tables XVII, XVIII, XIX, and XX. Results for these runs were plotted in purple ink upon the same Figures III to XIV inclusive which show curves





for the carbonization results on fresh coal. Comparisons may thus be made at a glance.

Gas data for the carbonization run on the residue from extraction of coal with xylene-selenium oxychloride mixture were also plotted on Figures III, IV, and V in red ink. Comparative results of these runs with those on fresh coal show the following:

Coke - There was no coke residue formed from carbonization of the residues from the selenium oxychloride extraction. The residues left in the retort were all powdery and had the same appearance as the original charge. The reagent entirely destroyed the coking property of the coal, either through extraction of the bonding material or through oxidation of the coal mass. The average percentage of residue left in these runs was 67.90 which is 4.20% less than the average coke residue from the runs on fresh coal.

Tar - There was no sign of tar distilled from the residues. Selenium oxychloride removes the tar forming constituent of the coal entirely.

Water - Not as much water distilled into the tar trap as during carbonization of the fresh coal. The temperature of heaviest distillation of water was from 210'-225'C. which is about 60'C. lower than the average maximum distillation point for water of decomposition of the coal.

Time and Temperature - Figure III shows the curve for Run 9 with a wide variation from Runs 10, 11 and 12. Run 9 was the only one of the four made on 30 grams of residue. The others being made on less residue naturally reached a higher temperature in the same length of time. Curves for runs 6, 7, 8, and 9 all for runs in which 30 grams of charge was used, shows that the temperature increased



with the time approximately the same when coking fresh coal and solvent residue.

Time and Gas Volume - Figure IV. shows that the residue when coked under the same conditions gives off more gas in any certain length of time than does the fresh coal. The residue, which is cellulosic, is practically all gas forming material, and also there is much oxygen present in the residue, which accounts for the rapid evolution of gas and the large volumes. The curve for Run 10 shows that 15 grams of residue will give more than twice as much gas in a certain length of time than an equal amount of the fresh coal.

Temperature and Volume of Gas - Figure V. shows that the runs on residue numbered 10, 11 and 12 yielded more gas up to 500' than did the fresh coal.

Carbon dioxide - in the gas from the residues shows a large increase over the amount given off by the coal. This may show that the residue was fairly highly oxidized by action of the reagent, and that part of the oxygen was chemically held, or that the residue being mainly cellulosic in nature gives large amounts of  $\text{CO}_2$  upon thermal decomposition.

Oxygen - The residues gave off much more oxygen than the fresh coal. This would point to the fact that the residues absorbed oxygen during the extraction process in spite of precautions.

Unsaturated hydrocarbons and Benzene - are absent from the gas. The reagent entirely removes these constituents from the coal.

Carbon Monoxide - is present in much larger amounts in the gas from the residues. Decomposition of cellulosic material and  $\text{CO}_2$  would account for this increase.





Paraffin hydrocarbons - Methane and ethane occur in somewhat smaller amounts in gas from the residues. The maximum point of their distillation is reached at from 50'-100' higher temperature than from distillation of coal. It seems that these gases are two of the last to come over from carbonization of the residues up to 625'C. The residue which is mainly cellulosic thus yields these saturated hydrocarbons.

Hydrogen- shows larger percentages at lower temperatures than from the fresh coal, and also increases more gradually so that at 600' slightly less hydrogen is evolved from the residue than from the coal.

#### VII. Conclusions, Part II.

Selenium oxychloride attacks coal in proportion to the amount of resinic volatile or tar forming content of the coal. Partially coked coal loses little, and coke nothing upon extraction. The reagent removes those resins and unsaturated hydrocarbons which form the tar upon distillation of coal. The extract or tar material is not separated pure, but enters into a chemical union with the reagent forming new compounds.

Selenium oxychloride reacts more completely with powdered coal with the evolution of heat. The action is not a solvent one, but a chemical reaction. All resinic and tar forming material of the coal is removed and changed by the reagent. The cellulosic portion of the coal is left unharmed. Selenium oxychloride removes a larger portion of the resinic constituent of the coal than do ordinary organic solvents.

No quantitative extraction is possible. A portion of the reagent is decomposed resulting in the deposition of red selenium



throughout the extract solution and residue. The residue may be purified from most of the selenium, but isolation of the extract is impossible.

Extraction is carried out to the best advantage without the use of external heat. Ordinary solvent extraction methods are not applicable to this work. The use of some solvent like benzene is necessary to aid in the separation of the residue.

Selenium and chlorine are present in the residue.

The ash of coal does not seem to be changed to any marked extent by the reagent. Nitrogen and Sulfur do not show an appreciable change. It should not be concluded from this that the nitrogen and sulfur are not affected, since the reagent in taking out the resinic material should remove some of these two constituents.

Paraffin hydrocarbons of the coal are probably not attacked.

The residue gives off much more oxygen than the coal. This may be due to oxidation of the residue and absorption of much oxygen which is not chemically held.

The presence of oxygen together with the loss of resinic material of the coal entirely removes the coking property of the coal.

Carbonization of coal residues after extraction with selenium oxychloride shows no sign of tar as one of the products of carbonization.

Selenium oxychloride divides coal into a cellulosic residue which yields gas chiefly, and a resinic portion which is extracted and which contains the tar forming bodies. The resinic portion also contributes to the yield of gas altho in not quite such large amounts as does the cellulosic residue. The cellulosic portion begins to decompose upon heating before the resinic portion has reached a





temperature high enough to decompose, that is, before the tar and gas yielded from the resins begins to distil. The formation of tar and decomposition of the resinic material in coal results in a rapid increase in the yield of gas, and if at this time, the cellulosic portion does not give off such gases as CO, CO<sub>2</sub> and O<sub>2</sub> in such quantities as to prevent bonding, the coal mass will begin to coke.

The residual cellulosic portion of coal upon carbonization yields, up to the temperature of secondary decomposition, as much or even more gas than did the original coal at the same temperature. This gas when analyzed shows presence of those gases resulting from decomposition of cellulose plus the paraffin hydrocarbons and large amounts of oxygen. No gas of an unsaturated nature or those formed from them are present.

#### VIII. Summary.

Selenium oxychloride attacks finely powdered coal with the evolution of heat. The amount of reaction is proportional to the volatile content of the coal. Coke loses nothing by attack.

Selenium oxychloride reacts chemically with coal and thus is not a true solvent. It may be used however in order to obtain a residue.

No quantitative extraction is possible due to decomposition of the reagent and its chemical reaction with the tar.

Neutral solvents, such as xylene, are not applicable for use with selenium oxychloride in coal extraction work.

Selenium oxychloride divides coal into two main portions, the cellulosic residue, and the resinic substances which are extracted. The extracted material consists of the tar forming



and part of the gas yielding constituent of the coal which is resinic or bituminic in nature. The residue consists of the cellulosic portion of the coal together with the ash or mineral matter. This cellulosic residue is primarily gas forming, yielding such gases as carbon monoxide, carbon dioxide, hydrogen, oxygen, methane and water of decomposition. The extracted constituent reacts with the reagent to form new complex compounds.

The residue when submitted to low temperature carbonization does not coke.

No tar is obtained from carbonization of the residual material. Selenium oxychloride removes the tar entirely from the coal, by extraction of the tar forming constituents.

Selenium and chlorine are present in the residue to a small extent.

Hydrogen of coal is given off in largest quantities between 350° and 575°C and not at either the beginning or end of the low temperature period.

Methane is given off by distillation of the cellulosic constituent of coal.





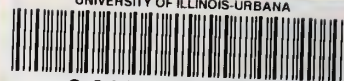
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